AN INTEGRATED STUDY ON THE IMPACT OF METALLIC TRACE ELEMENT POLLUTION IN THE COEUR D'ALENE-SPOKANE RIVERS AND LAKE DRAINAGE SYSTEM

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Additional funding was made available by the WSU Civil and Environmental Engineering Department and the Nuclear Radiation Center. University of Idaho funds were made available through the College of Letters and Science, Department of Biological Sciences.

Cover page organisms are diatoms recovered from core sediments of Lake Coeur d'Alene.

ABSTRACT

Comprehensive limnological, water quality, productivity and substrata investigations have been made of the Coeur d'Alene drainage, Coeur d'Alene Lake and the Spokane River. These investigations were made in an attempt to answer questions as to the passage of metallic elements through the aquatic food chain in the study area as well as to determine the critical factors involved in the poor recovery of the South Fork and main stem of the Coeur d'Alene River. Additional work was carried out to determine the water quality of these areas and the Spokane River. Extensive studies were also made upon the substrata and limiting factors for macroinvertebrates of the Upper Spokane River.

Artifical substrates (baskets) placed in the unpolluted portions of the Coeur d'Alene River developed abundant and diverse macroinvertebrate fauna comparable to that collected from natural substrata by Surber Sampler.

Flooding of Coeur d'Alene River during the spring highwater period transports heavy metals, especially Zn, into the lateral lakes bordering the river. Zinc concentrations in the lake water were highest near the lake inlets.

Metal concentrations in fishes from the lakes were higher than those tested from a control lake in the St. Joe drainage. There appeared to be greater Zn concentrations in the muscle tissues of omnivorous fish such as the bullhead than in the same tissue of piscivorus fish such as the large mouth bass. The fishes seem to be exerting some homeostatic control over the metal level in their tissues.

The overall water quality of Coeur d'Alene Lake appeared to be relatively the same as the found in our earlier study (Funk, Rabe, and Filby et al., 1973) based upon routine water sampling during coring operations and on data gathered from a water quality station maintained at the lake outlet.

Nineteen sediment cores were obtained along the lengthwise axis of the lake and from selected bays. A layer of heavy metals 80-30 cm in thickness occurred in the Coeur d'Alene delta region and lake proper. This layer decreased in thickness as one traversed the lake from off the delta region toward the outlet where the layer is reduced to 5 cm. Coring operations from the delta region of the lake toward the southern end revealed the same phenomenon occurred to a lesser extent to a point between the area of Conkling Park and Chatcolet Lake. This layer of heavy metals could constitute a hazard to aquatic life if Coeur d'Alene Lake eutrophies to the point of anaerobic conditions in the hypolimnion.

The biological productivity of the Spokane River is largely controlled by the water quality of Coeur d'Alene Lake as well as by the substrate, temperature and flow of the river. Nutrient additions to the river as it flows toward the city of Spokane increases the productivity of the lower four stations, especially at the Plantes Ferry station.

Heavy metals, such as Zn, Cu, and Pb, appear to be concentrated to relatively high amounts in algae, aquatic macrophytes and other vegetation growing along the river. Algae and detritus-consuming macroinvertebrates such as mayfiles and stoneflies pass these metals along to the fishes, expecially trout because of the trout's predilection for these organisms. However, there appears to be a reduction of concentration of metals in tissues at each trophic level as one moves up the food chain. The organisms appear to be actively excreting the metals. In the fishes, the filter bodies such as the kidneys and liver concentrated the metals several-fold over that of other tissues and therefore tend to confirm this assumption. Nonetheless, the level of Zn, for example, in the muscle tissue of Spokane River fishes may be two to three times that in muscle tissue of the same species taken from undisturbed streams high in Coeur d'Alene drainage. For these reasons it has been concluded by the investigators that additional efforts should be made to curtail and control seepage from tailings ponds as well as reduction and eventual control of wastes and nutrient runoff in the Coeur d'Alene and Spokane river drainage basins. The area encompassed by this study includes extremely valuable recreation, wildlife, and fisheries recources as well as sources of food and water for human consumption.

FCST Category V-A, V-B, V-C

Keywords: Trace Metals, Concentration of Trace Metals by Organisms, Aquatic Food Chain, Neutron Activation Analysis, Coeur d'Alene Lake Drainage System, Spokane River Drainage System, Uptake of Zinc by Sediments, Sensing Trace Metals, Water Quality.

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INTRODUCTION

Objectives

We entered this research project with the overall objective of pursuing an intensive and comprehensive investigation of the Coeur d'Alene River and Lake as well as the upper Spokane River. In order to accomplish such a large task, we enlisted the cooperation and expertise of two major universities, three colleges, three research centers and four departments. We were also very fortunate in securing the cooperation of the U.S. Bureau of Fisheries and Wildlife, U.S. Geological Survey, Washington Water Power Company, the Washington State Department of Ecology and the Washington State Bureau of Wildlife Management.

In the first phase of our study (OWRR Title I B-044 WASH and B-015 IDA), our major efforts were devoted to determining the overall biological productivity and water quality of Coeur d'Alene Lake and the upper Spokane River. We also completed a preliminary assessment of the effect of metallic and organic pollution in the Coeur d'Alene River and the upper Spokane River including an initial assessment of the concentration of several metallic elements in the bottom sediments, selected benthic organisms, and several non-game varieties of fishes.

The specific objectives of this research project were:

1. To monitor the water passage of metallic trace elements through the Coeur d'Alene River-Lake/Spokane River system by atomic absorption and neutron activation methods.
2. To attempt to determine the critical factor(s) inhibiting further recovery of the benthic macroinvertebrate fauna of the South Fork and main stem of the Coeur d'Alene River.

3. To assess the concentration of trace metallic elements at different trophic levels (emphasizing fish as the highest food chain level) throughout the Coeur d'Alene-Spokane River systems.
4. To continue water quality monitoring of the upper Spokane River to obtain data for usage by State and Federal agencies and for possible comparison or incorporation into water quality models of that area.

As a result of our Title I study and earlier work by Savage and Rabe (1973), we realized that the reduced turbidity of the Coeur d'Alene River (accomplished by construction of tailings ponds) had resulted in the growth of large masses of attached periphyton in certain areas of the river channel. Savage also brought to our attention that two species of chironomids and one other dipteran species had begun to colonize these areas despite the high metallic content of the waters. We therefore wanted to investigate the nature of the substrata and the nutrient levels of the water in an attempt to resolve the growth-limiting factors in this area.

Lateral Lakes of the Coeur d'Alene River

Few previous studies have considered the lateral lakes along the Coeur d'Alene River. Notable exceptions have been Ellis (1932), who observed that three of these lakes (Swan, Thompson and Blue) apparently were affected by toxic materials. Ellis found that they supported no plankton or benthic organisms, while the remaining lakes did support these organisms as well as fish. Chupp and Dalke (1964) studied waterfowl mortality in the areas along the river and concluded after analysis of plants, soils and waterfowl tissues that the heavy metal pollution from mining wastes was the primary cause of bird losses along the river.

For these reasons we conducted extensive studies of these lakes to determine the heavy metal content of the upper sediments as well as the biological concentration of the metals in fishes common to the lakes.

Coeur d'Alene Lake

In our earlier Title I study, comprehensive data were taken on water quality, phytoplankton productivity, benthic invertebrate populations; we also analyzed five sediment cores obtained near the Coeur d'Alene delta area. It was felt that this latter portion of the study should be expanded to gain an insight into the overall depth and concentration of metallic elements deposited along the lengthwise axis as well as in the major bays and mouths of tributaries entering the lake. Dunigan (1972) made preliminary sedimentation calculations based on the delta cores. These additional coring data now can be used to calculate sedimentation rates in other areas of the lake. Sheppard and Funk (1975) analyzed tree rings taken from the vicinity of the upper Spokane River by neutron activation methods. These data were compared to Dunigan's data and subsequent core data. Interestingly enough, it was found that many of the core peaks corresponded with peaks in the tree rings and also with mining activity records. Another facet of this study was an attempt by members of the study team to better define by laboratory study the mechanism for adsorption of zinc ions on clay structures.

Upper Spokane River

Our previous study indicated that the water of the upper Spokane River is generally of good to excellent quality in all parameters tested except for a high metallic content, especially zinc. Activation and atomic absorption analysis of the metallic content in tissues of the organisms populating the Spokane River indicated that the algae were prime concentrators of zinc, cadmium, lead, mercury, iron and manganese. Algae and detritus consumers,such as the larvae of the caddis fly Hydropsyche and the nymphs of the mayfly Baetis, reflected high metallic concentrations. Most higher aquatic plants showed relatively lower concentrations. Analysis of non-game fish tissues showed a considerably lesser concentration of metals than the aquatic plants, insects or algae. However, liver tissue concentrations in these fishes ranged from 80 to 200 mg/kg while muscle tissues were considerably lower, ranging from 33 to 54 mg/kg.

It was decided to carry out testing on game species of fishes as well as continuing water quality testing, including heavy metals analysis.

We were also interested in determining the metallic content in the tissues of fishes residing in the Coeur d'Alene lateral lakes region. In addition, with the cooperation of the Federal Fish and Wildlife Service, we were able to obtain game fishes from drainage areas above those affected by mine effluents in the Coeur d'Alene area for comparative testing of metallic concentration in tissues.

It was thought also that coring of the Spokane River should be attempted again in order to define the metallic content of sediments downstream from Coeur d'Alene Lake. Multiple-plate colonizing devices similar to those of Hester and Dendy (1962) and Fuller (1971) were set out to aid in defining food chain sources in the river. One comprehensive macrobenthic survey was carried out to gather additional information on benthic invertebrate populations.

Study Team Personnel

Washington State University personnel: Dr. William H. Funk, Environmental Engineering, in charge--coordination of Coeur d'Alene Lake cores collections, Spokane River studies and project coordination.

Mr. Gary Bailey, M.S.--in charge of fish collection and field chemical analysis for Spokane River studies.

Mr. Paul Bennett, B.S.--in charge of chemical analysis by atomic absorption of fish tissues and water samples.

Mr. Gerald Bannon, B.S.--graduate student, aiding in fish tissue analysis by neutron activation and in charge of productivity studies, Spokane River.

Mr. George Edwards, B.S.--graduate student, aiding in field chemical analysis and in charge, field macroinvertebrate surveys, Spokane River.

Dale Anderson, B.S.--graduate student, in charge of total organic carbon (TOC) analysis of sediment cores.

Mr. Pat Syms--research technician in charge, sediment core collection.

Dr. Royston Filby--in charge, coordination of neutron activation analysis of fish tissue and sediment samples at Washington State University Nuclear Radiation Center (WSU NRC).

Kishor Shah, M.S.--supervision of sample preparation and analysis (WSU NRC).

Alain Bourg, M.S.--graduate student, in charge of laboratory experiments in relation to Zn uptake by clay minerals.

Ms. Jane Rothert--graduate student, aiding in neutron activation analysis and trace metal experiments.

Alan Seamster--undergraduate assistant, working on tissue and sediment analysis (WSU NRC).

Dr. John C. Sheppard--in charge tree ring analysis, Department of Chemical and Nuclear Engineering.

University of Idaho Personnel: Dr. Fred W. Rabe, Department of Biological Sciences, in charge--coordination of Coeur d'Alene river and lateral lakes studies.

Ms. Nancy Savage, M.S.--in charge, macroinvertebrate and substrate studies in Coeur d'Alene River and consultant for macroinvertebrate studies in the Spokane River.

Mr. Steve Bauer, B.S.--graduate student in charge, heavy metal analysis of sediments and fish tissues taken from Coeur d'Alene River and lateral lakes area.

DESCRIPTION OF THE STUDY AREA

Geography

The basin containing Coeur d'Alene Lake is a submerged river valley 38.6 km (24 mi) long with an average width of 1.6 km (≃1.0 mi) and is located in Kootenai and Benewah Counties of northern Idaho. The present elevation of Coeur d'Alene Lake is maintained by Post Falls Dam on the Spokane River. The southern portion of the lake is divided into three shallow lakes--Chatcolet, Benewah and Round--which were created in 1906 by the erection of the dam. The depth gradually increases toward the northern end of the lake to a maximum of 54.9 m (180 ft) off Three Mile Point in the northern narrows.

Two major rivers, the Coeur d'Alene and St. Joe, discharge into the southern portion of the lake. The headwaters of both rivers originate in the Bitterroot Range between Montana and Idaho. The Coeur d'Alene River drainage basin, an area of approximately 10,360 sq km (≃4,000 sq mi), consists of two subdrainages, the South Fork draining the Coeur d'Alene mining district (Figure 1) and the North Fork in the Coeur d'Alene National Forest. The South Fork joins the North Fork at Enaville to form the main stem of the Coeur d'Alene River, which flows 48.2 km (30 mi) west into Coeur d'Alene Lake at Harrison, Idaho. The St. Joe River, with a watershed of about 3,880 sq km (≃1,500 sq mi), is free of mine wastes but has been affected to some extent by sewage disposal, logging and farming activities.

The Spokane River, the only surface outlet of the lake, flows westerly from the northern end of the lake, then through the city of Spokane, Washington (pop. 200,000) to its confluence with the Columbia

River 160.9 km (100 mi) to the southwest. The Spokane River above Spokane, the St. Joe River and the North Fork of the Coeur d'Alene River support excellent sport fisheries, while the South Fork and main stem of the Coeur d'Alene River and the Spokane River below Spokane have serious pollution problems and a reduced diversity of biota.

The study area is shown in Figure 1.

Geology

Pre-Cambrian metasediments underlie most of the Coeur d'Alene and St. Joe drainage basins. Faulting and subsequent mineralization in portions of this area have resulted in deposition of valuable minerals including sulfides of lead, zinc, silver and antimony and smaller quantities of copper, cobalt and gold. The Coeur d'Alene mining district--adjacent to the South Fork of the Coeur d'Alene River--produces most of the United States' supply of antimony and zinc and much of its silver. The lower reaches of both rivers, the lake and the Spokane River have been eroded in Miocene basalts which overlie the basement complex; the basalts in turn are overlain by glacial alluvium or windblown loess deposits of post-glacial origin (Ross and Savage, 1967).

Sources of Pollution

Since 1885, waste material from the Coeur d'Alene mining district has been carried into the lake. Tailings from ore-crushing mills have been a source of large amounts of rock flour. Subaerial oxidation of heavy metal sulfides in exposed tailing ponds and subsequent leaching have contributed ions of heavy metals to streams and ground water. Effluents from lead and zinc smelters have contributed particulate

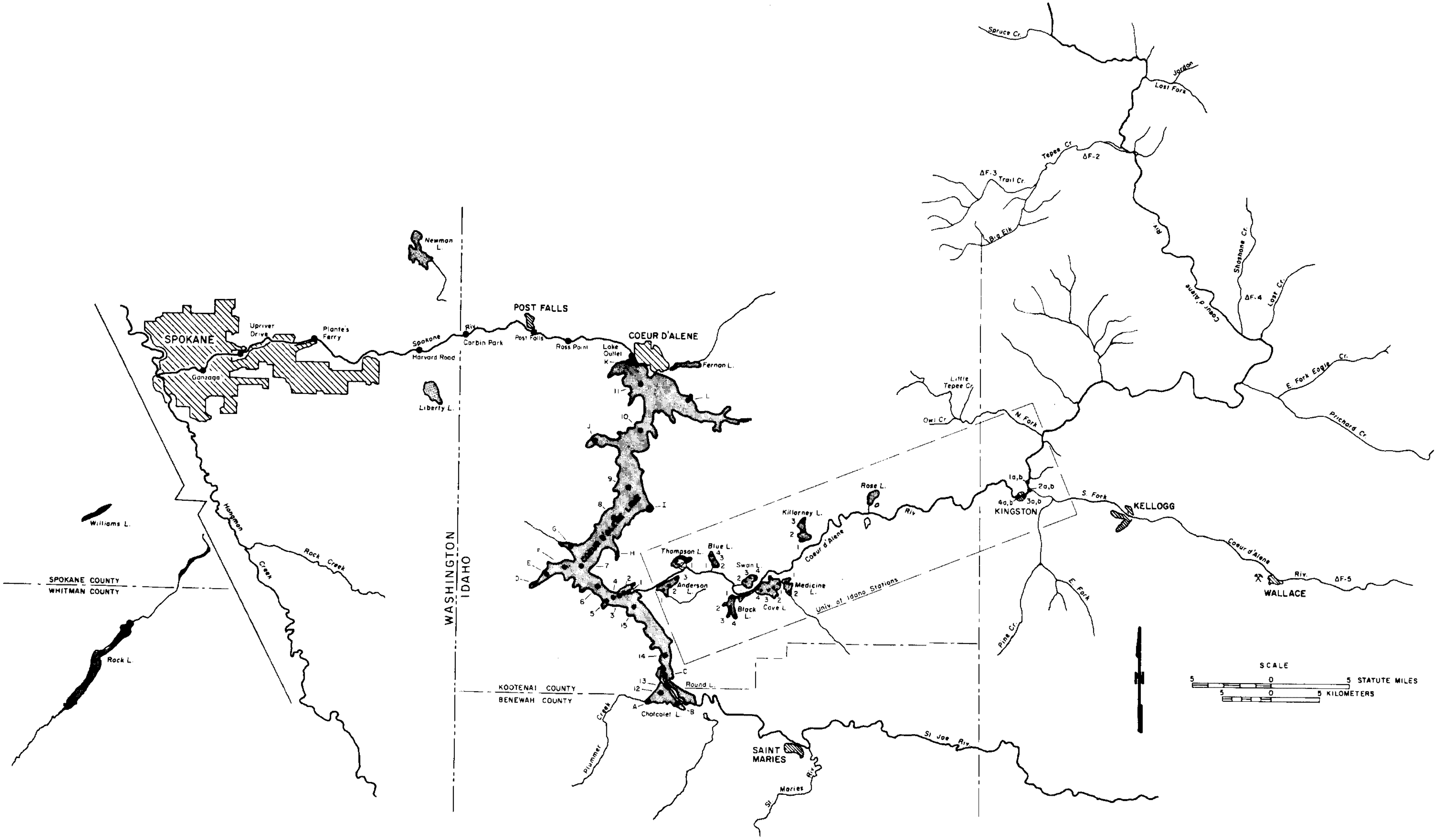

Figure 1. The Study Area

matter and heavy metal ions to both air and water. A study conducted in 1911 indicated a reduced plankton population in the Coeur d'Alene River delta as compared with the open waters of the lake (Kemmerer et al., 1923). An extensive survey by Ellis in 1932 showed the river to be devoid of life from the city of Wallace to its mouth, and the delta to be deficient in plankton, fish and bottom organisms. Assay tests conducted by Ellis on native fish species indicated that lethal concentrations of zinc ions were present in the river. Sappington (1969) found a 96-hour TL_m (median tolerance limit) of .09 mg/1 Zn for Cutthroat trout fingerlings using water from the North Fork treated with known amounts of $ZnSO_4$. Zinc concentrations as high as 2.6 mg/1 at the river mouth and 21 mg/1 in the lower reaches of the South Fork were reported by Mink et al. in 1971.

The river depth has been decreased by siltation (Figures 2, 3 and 4), and large volumes of rock flour have been carried out over the lake since the beginning of mining operations in this area. Not until the construction of settling ponds in 1968 to impound ore-mill wastes has any reduction in silt load been accomplished. Evidence of mine tailings and unusually high concentrations of Zn has been detected throughout the lake by our earlier study (Funk, Rabe, Filby et al., 1973) and several others (Sceva and Schmidt, 1971; Stokes and Ralston, 1971).

Population increases and lack of adequate sewage treatment facilities in the towns along the Coeur d'Alene and St. Joe Rivers and at shore dwellings have permitted untreated and partially treated sewage to enter the lake (Leeright, 1971); (Flaherty, 1972), as indicated by the extensive growth of blue-green algae and macrophytes in shallower areas of the lake. Silt and nutrients from cultivated lands also appear to provide a substantial nutrient input into the southern portion of the lake. Near the lake outlet and along the western shoreline, large log rafts (Figure 5) await movement to sawmills. The lake bed in these areas is covered with bark and wood chips. Figure 6 shows the submerged St. Joe River channel. Figure 7 shows the main body of Coeur d'Alene Lake. Figure 8 shows the lake outlet and headwaters of the Spokane River.

Figure 2. The Valley of the South Fork of the Coeur d'Alene River. Extensive Settling Ponds now Reduce Transport of Silts to the River. River Flow is Toward the Viewer.

Figure 3. Coeur d'Alene River Channel and Delta. The Channel has Extended Itself Some Distance into the Lake by Siltation.

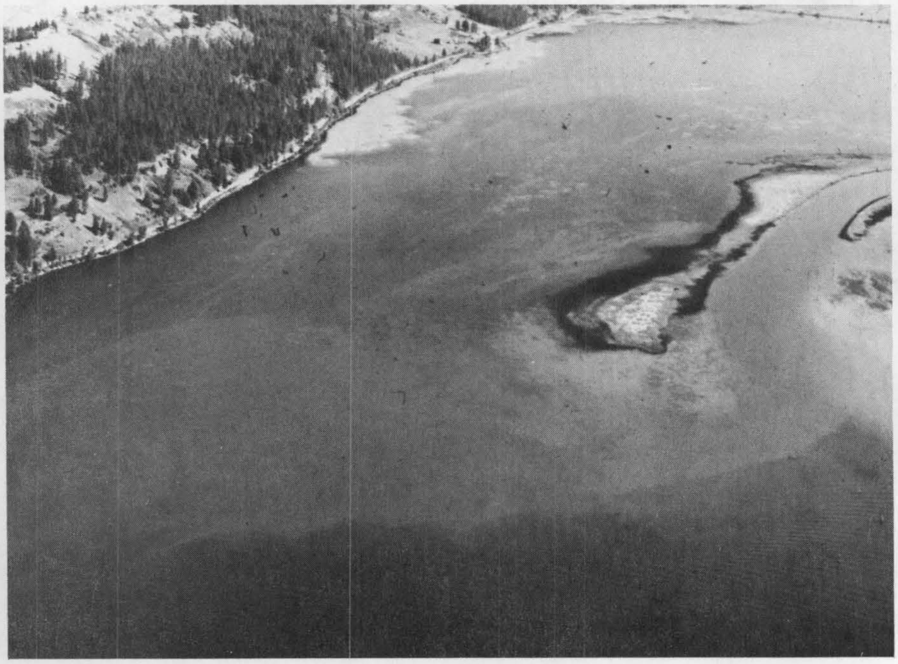

Figure 4. Upstream View of the Channel. An Extensive Silt Load is Still Carried by the River.

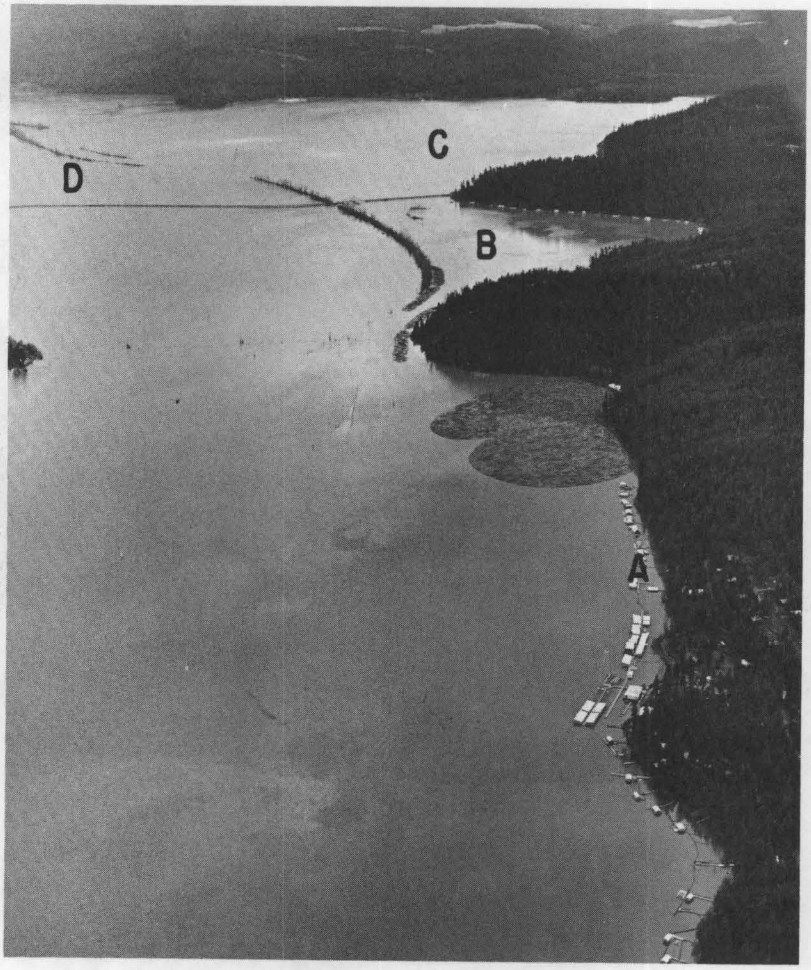

Figure 5. Log Rafts Stored Near Conkling Park, Area A. Area B is Hidden Lake, Area C is Chatcolet Lake, and Area D is Round Lake of the Southern End of the Coeur d'Alene Lake System. (Note the Extensive Use of the Shoreline for Boat Houses, Summer Homes and Other Recreational Purposes.)

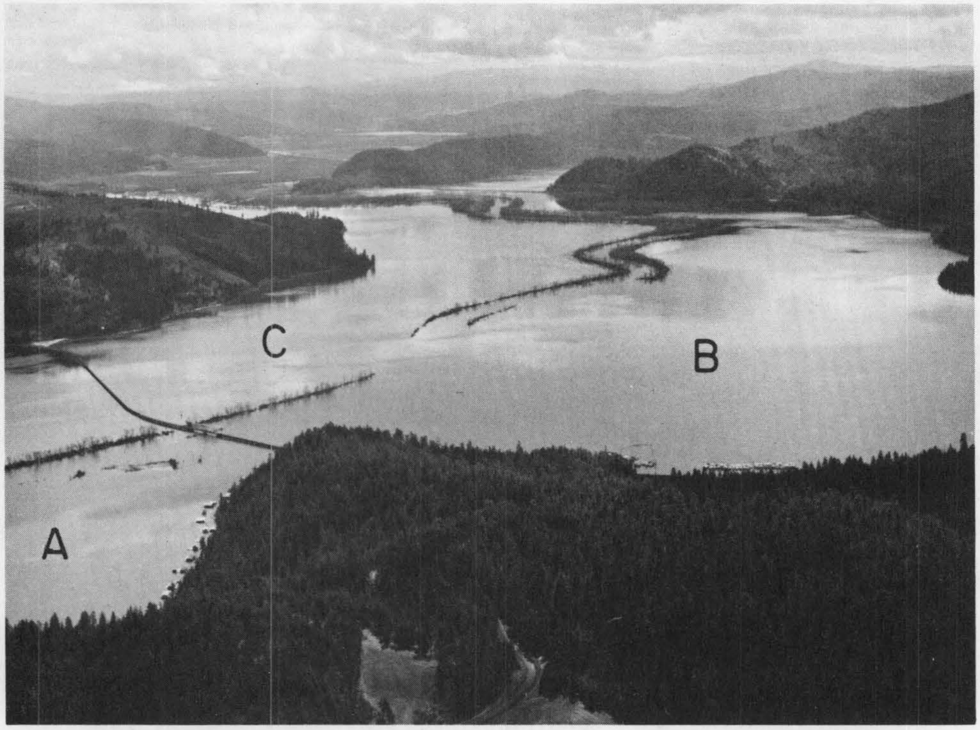

Figure 6. Southern End of Lake Coeur d'Alene Showing Submerged St. Joe River Channel. Area A is Hidden Lake, Area B is Chatcolet, Area C is Round Lake.

Figure 7. Main Body of Coeur d'Alene Lake. The View is North Toward the City of Coeur d'Alene.

Figure 8. Coeur d'Alene Lake Outlet and the Head of the Spokane River. Letter A Indicates Coeur d'Alene City Sewage Plant, B Indicates the Spokane Yacht Club, and C, D, and E are Industries Along the Spokane River. Flow of River is Away from the Viewer.

Sampling Sites

To insure proper handling of samples in field preparation and laboratory analysis, each sampling area was assigned a location, sample number or both. For report clarification and rapid identification of location these have been reduced for inclusion in Figure 1. For further clarification, expanded diagrams are shown in the Results and Discussion Section when deemed necessary. The Coeur d'Alene River stations are shown as North Fork (1a) and (1b), South Fork (2a) and (2b), etc. to distinguish between riffle, pool and glide areas (Figure 1). The lateral lakes area is shown by lake name and location within the lake by number such as Cave Lake (1), (2), (3), (4), etc. (Figure 1).

Coeur d'Alene Lake stations are shown in Figure 1 by a consecutive number for the lengthwise transect coring operations and alphabetically for the bay regions. Coring numbers continue consecutively from #5 delta region (last station) reported in our previous study (Funk, Rabe, Filby *et al.*, 1973). The Spokane River stations are identified by river mile and location. Coring or dredge samples were obtained at the same stations. The Spokane River fish collections were made at two of these stations. Collections contributed by U.S. Bureau of Fisheries and Wildlife are shown by location and designated numbers as F-1 and F-2, etc. (Figure 1).

MATERIALS AND METHODS

Physical Measurements

Temperature

River and lake temperature series were measured by Yellow Springs Instrument Corporation (YSI) probes (±.6 C), Whitney Thermistors Model TC-5 (±.01 C), or an Applied Research Associates' electric thermometer (±.1 C). On occasion, a Van Waters and Rogers ASTM-1C partial immersion mercury thermometer was utilized (±0.5 C).

Light

Light penetration was measured by a Secchi disc and a Gemware submarine photometer; in the latter case, electrical units were recalculated to standard foot-candles.

Depth

Depth soundings were made with a Raytheon DE-735 Fathometer System utilizing a Raytheon DE 7041 Transducer (0-202.8 m ±.5%).

Field Chemical Measurements

Alkalinity

Alkalinity was determined by methods described in the American Public Health Association's *Standard Methods for the Analysis of Water and Waste Water*, 13th Ed. (referred to in following citations as APHA-Standard Methods), utilizing phenolphthalein and methyl orange as indicator solutions.

Dissolved Oxygen

Dissolved oxygen was determined by YSI probe (±.25 mg/l). Comparative measurements also were made using the azide modification of the Winkler Method as suggested by APHA-Standard Methods (1971). The Winkler Method was also substituted in instances of probe failure.

pH

Measurements of pH were made with Beckman Model N battery-operated pH meters (±5%) and in some instances with a Hellige pocket comparator.

Conductivity

Conductivity measurements were made with an Industrial Instrument-RB-SOLU Bridge conductivity meter (±5%).

Field equipment and instrumentation are shown in Figures 9, 10 and 11.

Laboratory Chemical Analysis

Water samples were collected from various depths in the rivers and lakes using Van Dorn water bottles or a weighted continuous pump sampler (Figure 9). In some cases, grab samples were made along the rivers. In each instance, the samples were placed in 1.0-liter polypropylene bottles and cooled to 4.0 C in ice chests.

Standard chemical analyses (wet) were carried out at the WSU Environmental Engineering laboratories primarily utilizing a Technicon Autoanalyzer II equipped with modules to measure specific water quality parameters described in subsequent pages. A back-up system was maintained utilizing a Beckman DU-2 spectrophotometer equipped with a photomultiplier

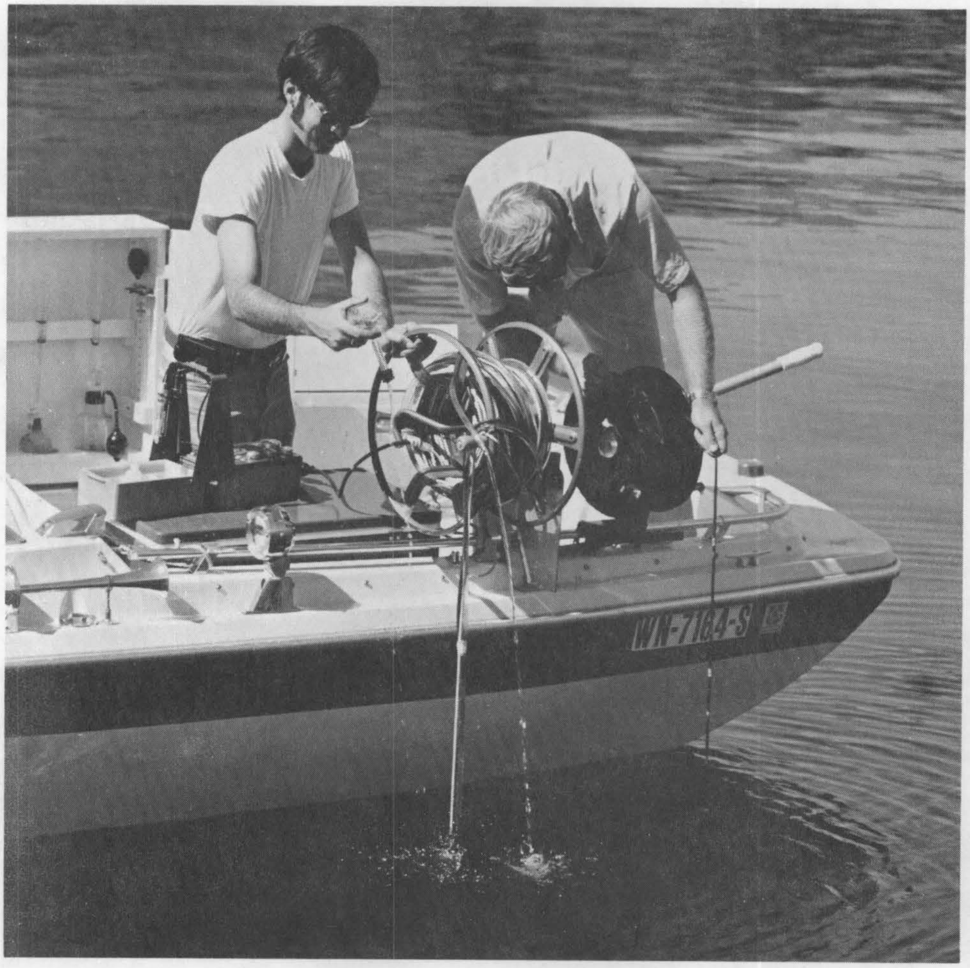

Figure 9. Field Sampling and Testing Equipment Aboard Washington State University's Research Boat.

Figure 10. Collecting Water Samples off Coeur d'Alene, Idaho.

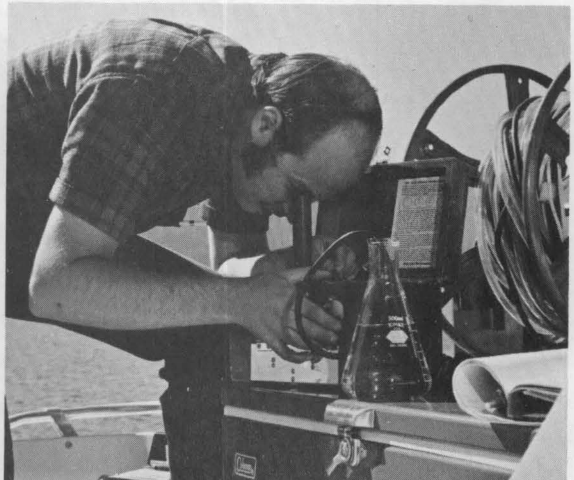

Figure 11. Immediate Analysis of a Water Sample Aboard Research Boat.

unit. Total organic carbon in sediments was measured with an Oceanography International Total Carbon System equipped with both ampoule and direct injection modules. Atomic absorption techniques were used in conjunction with Perkin-Elmer 303 atomic absorption spectrophotometers to determine certain metallic constituents of the water samples.

Analytical methods generally followed those procedures set forth by Technicon Autoanalyzer II Methods Manual (TAA), APHA-Standard Methods (1971), the Environmental Protection Agency's (EPA) Methods for Chemical Analysis of Water and Wastes (1971), EPA-Analytical Methods Manual for Bottom Sediments (Great Lakes Committee, FWQA, 1969) and Oceanography International Instruction and Procedures Manual for the Total Carbon System (1973). The brief description which follows indicates the primary method selected.

Total Phosphate-Phosphorus

Total phosphorus was measured by TAA II Methods (116-71W) based upon the digestion of particulate and organic matter in water followed by standard methods of ortho-phosphorus measurement utilizing ammonium molybdate and amino-naphthol sulfonic acid reagent, which react with phosphorus to form a blue phosphomolybdenum complex whose intensity depends upon the quantity of phosphorus present.

Orthophosphate-Phosphorus

Ortho-phosphorus was determined by TAA II Method (155-71W) utilizing a single reagent solution of acidified ammonium molybdate and a small amount of antimony potassium tartrate. The phosphomolybdenum blue complex is read colorimetrically at 880 nm (Murphy and Riley, 1962).

Total Nitrogen (Kjeldahl)

Total nitrogen (Kjeldahl) was determined by TAA II Method 146/71A using the Technicon Continuous Digestor followed by measurement of the quantity of ammonia produced. The quantitation of ammonia is achieved by means of the Berthelot Reaction, in which formation of a blue indophenol complex occurs when ammonia is reacted with sodium phenate followed by the addition of sodium hypochlorite (Van Slyke and Hiller, 1933).

Ammonia in water also was determined by the Berthelot Reaction utilizing TAA II Method 98-70W with the addition of potassium sodium tartrate to eliminate precipitation of the hydroxides of heavy metals (Bolleter, *et al*., 1961; Tellow, J., and Wilson, A., 1965).

Nitrate and Nitrite-Nitrogen

Nitrate and nitrite nitrogen was determined by the reduction of nitrate to nitrite by a copper cadmium reductor column (TAA Method 100-70W) (Armstrong, Sterns and Strickland, 1967). The nitrite ion then reacts with sulfanilimide under acidic conditions to form a diazo compound. This compound then reacts to form a reddish purple color. Divalent copper and mercury may form a color complex in the region of color measurement, thus making a positive error in analysis (FWPCA, 1969).

Sulfate

Sulfate was determined by TAA II Method 118-71W by passing the water sample through a cation exchange column to remove interferences. The sample next is reacted with barium chloride at pH 2.5-3.0. The excess barium reacts with methylthymol blue to form a blue-colored chelate at a pH of 12.5-13. Uncomplexed methylthymol blue measured at 460 nm is equal to the amount of sulfate present (Lazrus *et al*., 1965).

Chemical Oxygen Demand

Chemical Oxygen Demand (COD) was measured by TAA Method 137-71W based upon APHA-Standard Methods (1965) and Molof and Zaleiko (1964) in which the sample is digested with potassium dichromate sulfuric acid and the depletion of the hexavalent chromium due to the oxidation reaction is measured colorimetrically.

Biochemical Oxygen Demand

The procedures outlined by APHA-Standard Methods (1971) were followed. The bottles were submerged in 20 C water bath and incubated in a thermostatically controlled darkroom.

Total Organic Carbon

Total Organic Carbon (TOC) in water was measured by collecting water samples in 300ml glass stoppered bottles (which had been pretreated at 550 C). The samples were fixed with $HgCl_2$, and transported to the WSU Environmental Engineering laboratories, and 10ml subsamples were sealed in ampoules within 36 hours. The ampoules were cleaned and combusted at 550 C for 4 hours prior to usage. Two-tenths ml of 8% phosphoric acid was added to each ampoule prior to sealing; then they were heated at 175 C in a pressure vessel for 8 hours. After cooling, the ampoules were broken and subsequent CO_2 was determined by infrared analysis utilizing an Oceanography International carbon analyzer and integration recorder. The quantity of organic carbon present in the water was calculated by French curve methods developed by the WSU Computing Center and Bannon (1974). Integration numbers for a series of standards and samples run concurrently on the infrared analyzer were used to fit a curve through a series of data points using cubic polynomial coefficients. The polynomial coefficients then were used in an additional program to calculate mg/l TOC utilizing an IBM 360/67 computer.

Hardness

Hardness was determined by the EDTA titrametric method outlined by APHA-Standard Methods (1971).

Iron

Procedures were followed as outlined by APHA-Standard Methods (1971) with the exception that acid pretreatment of samples was not made.

Neutron Activation Analysis

Neutron activation analysis was used to measure Fe, Co, Se, Hg, Cr, Rb, Cs, Th, Sb, Co, Zn, Sc and Eu in sediment, water and organism samples. The elements Al, V and Mn also were measured in some sediment samples.

Sediments and tissues (≈1.0 gm) were freeze-dried under dust-free conditions. The samples were sealed into clean, high-purity polyethylene vials (2 drams) and irradiated with standard solutions of the elements of interest (prepared from Johnson-Matthey "Specpure" materials). For the determination of Al, Mn and V in sediment samples, the samples and standards were irradiated for 5 mins in the WSU TRIGA-III-type research reactor in a thermal neutron flux of 8×10^{12} n/cm^2 sec. For Fe, Co, Cr, Rb, Cs, Se, Hg, Th, Sb, Co, Zn, Sc and Eu, an 8-hour irradiation in a neutron flux of 8×10^{12} n/cm^2 sec was used.

After irradiation, the samples were placed in concentrated HNO_3 for 4-8 hours to remove impurities adsorbed on the vial surfaces during immersion in the pool during irradiation. For Al, V and Mn, the samples were counted 5-20 minutes after irradiation. For the other elements, a 4- to 6-week decay period was necessary. A high-resolution Ge(Li) detector was used for γ-ray spectrometry of the irradiated samples. Gamma-ray spectra of samples and standards were recorded on magnetic tape and γ-ray peak areas calculated by the FOURIER program on the IBM 360/67 computer. Full details of the gamma-ray spectrometry and elemental concentration calculations are given by Filby *et al*. (1970) and Shah *et al*. (1970a, 1970b). Corrections were made for the elemental contents of the vials used in the irradiations.

Fish Tissue Analysis

Fish were collected by personnel from the University of Idaho, the U.S. Bureau of Sport Fisheries and Wildlife and Washington State University. The latter two groups tagged, froze and delivered the fish to the Environmental Engineering laboratories at WSU. The fish were unfrozen, weighed, measured and dissected with stainless steel knives under semi-sterile conditions. Portions of organs, such as the kidney, liver, fat and muscle tissue, were freeze- or oven-dried (105 C), digested by perchloric and nitric acids (Smith, 1955) (Leonard, 1972) and then analyzed by atomic absorption procedures. In certain instances, desiccated subsamples were delivered to the WSU Nuclear Radiation Center for additional testing for trace metals by neutron activation analysis.

Methods followed by the U of I Biological Laboratories for fish and benthic invertebrates collected in the lateral lakes and Coeur d'Alene

River areas differed slightly in perchloric-nitric acid digestion of the fish tissue and desiccating procedures (all were oven-dried). These methods followed those of Thompson and Blanchflower (1971), with modification as follows: Approximately 1.0 g dry tissue was digested in a mixture of 3 ml of distilled concentrated HNO_3 and 1 ml of 70 percent perchloric acid for 2 hours, then evaporated to near dryness, to which a fixed amount of 5 percent HNO_3 was added for dilution. Two reagent blanks were run with each sample set for correction purposes.

Fish were collected in all instances by gillnetting and angling. All game fish were collected in compliance with Washington and Idaho fisheries and game management collection permits. Fish-shocking methods of collection were employed in both collection areas but proved to be ineffective in the soft water (14-30 mg/1 $CaCO_3$--total hardness) of both the Coeur d'Alene and the Spokane River. A few fish also were collected from Coeur d'Alene Lake (for comparative purposes) by angling. Figures 12 and 13 show University teams collecting fish by gillnetting.

Aquatic Invertebrates

The trace metal concentration of these organisms was measured in the same manner as the fish specimens, with the exception that whole body analysis was made after a live holding period of up to 36 hours in order to clear the gut content.

Figure 12. University of Idaho Graduate Student Collecting Fishes from the Coeur d'Alene Lateral Lakes Region.

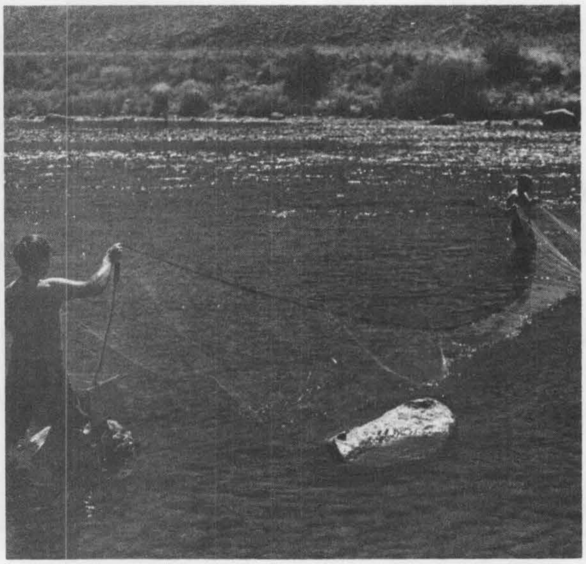

Figure 13. Staff Members of Washington State University set Gill Nets to Collect Fishes from Upper Spokane River.

Sediment Analyses

Analysis of Sediment Core Samples

Nine sediment cores were taken along a lengthwise transect across Coeur d'Alene Lake and 12 cores were taken in bays and adjacent lakes (Figure 1) to obtain materials for analysis of metallic constituents. Fifteen cores were attempted in the Spokane River, of which only one was partially successful. Sediment in this study area had to be obtained by dredging and diving because of the nature of the river bottom (Crosby, 1973).

The core samples were collected with a Ewing-type piston corer (Gemware) weighing 68 kg (150 lbs). The coring device was mounted on the WSU Environmental Engineering pontoon barge shown in Figures 14-17. Cellulose acetate liners--1.83 m (6 ft) long with a 3.5cm inner diameter--were inserted into the coring tube to retain the sediments.

After the cores were obtained, the cored samples in the plastic liners were stored at 4 C until they could be sectioned for analytical purposes. All samples except those portions used for pH, oxidation reduction potential (ORP) and neutron activation were dried for 24 hours in a 105 C oven. The samples used in neutron activation analysis were dried in a 75 C oven or freeze-dried. The pH and ORP were determined on undried samples at water saturation percentage. Prepared samples were analyzed with a Beckman Model 76 pH meter and ORP with a Leeds-Northrup pH meter. Percent water content was determined by weighing before and after drying in a 105 C oven for 24 hours.

Dried core sediment samples (.5-2.5 gm) were digested according to procedures outlined in Great Lakes Committee-Analytical Methods Manual for Bottom Sediments EPA 1969 and the resulting extract analyzed for total phosphorus and metals.

Figure 14. Coring Derrick and Ewing Piston Corer.

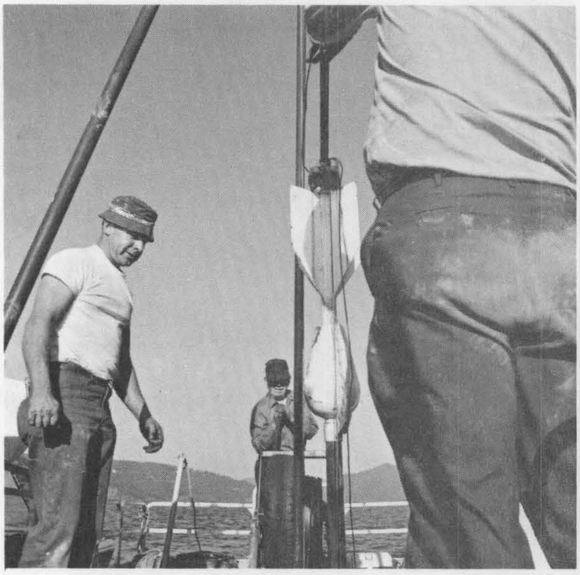

Figure 15. Lowering of Piston Corer through Barge Platform.

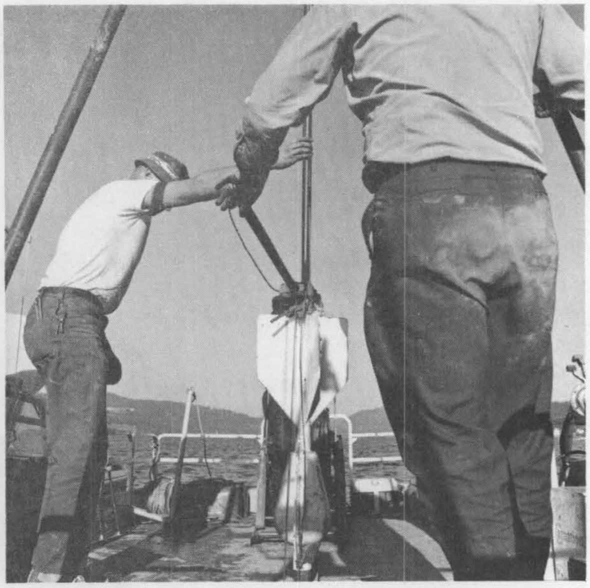

Figure 16. Activation of Trigger Mechanism of Corer.

Figure 17. Lowering of Coring Mechanism until Trigger Mechanism Activates Free Fall.

Total organic carbon was determined utilizing the Oceanography International Total Carbon System Ampoule Module method. In this system a sample (.1 g) of dried sediment is oxidized by potassium persulfate at temperatures exceeding 100 C and the resultant CO_2 measured by infrared analyzer. Our methods were developed by Anderson (1975) and consisted of first placing a core sample in a 105 C oven for 24 hrs and then grinding and homogenizing the sample by using an acid-washed mortar and pestle. A precombusted (heated to 500 C and cooled) ampoule was tared and a portion of the sample introduced. The ampoule was reweighed to the nearest .00001 g then .2 g of potassium persulfate, .025 ml of 8% v/v phosphoric acid solution and 10.0 mls of deionized distilled water were added. Ampoules were purged six minutes, then sealed and combusted at 175 C for approximately 12 hours.

Carbon standard integration numbers were plotted and a standard curve was generated using a French curve computer program. Sample carbon values were interpolated and final results calculated by use of another computer program similar to that utilized for the TOC analysis of water.

Sediment Samples for Lateral Lake Sediment Study

Samples for organic content and heavy metal analysis were carefully collected with an Eckman dredge to minimize disturbance of the substrate surface. Sediment from the top 3 cm was placed in sample bottles and stored under ice. Upon return to the laboratory at the University of Idaho, samples were homogenized by stirring with a glass rod before subsamples were extracted for analysis following the methods outlined in Analytical Methods Manual for Bottom Sediments (EPA, 1969). Subsamples were delivered to the WSU Environmental Engineering laboratories for freeze-drying and then to the WSU Nuclear Radiation Center for heavy metal analysis.

Biological Analyses

Macroinvertebrate Collection and Analysis

The Surber sampler and an artificial substrate sampler were employed in the Coeur d'Alene River to sample the benthic macroinvertebrate community. The Surber sampler (Surber, 1937) consists of a frame which encloses an area of substrate .09 m^2 (1 ft^2) in area and a 30-mesh net positioned downstream from the frame which retains organisms dislodged from the substrate within the enclosed area. Two Surber samples were collected and pooled at each station for each sampling period.

The artificial substrate samplers consisted of cylindrical wire barbecue baskets, 35 x 17 cm in size, filled with stones ranging from 8 to 12 cm in diameter (Figure 18). This basket has been described by Mason *et al*. (1967), Anderson and Mason (1968) and Fullner (1971) for sampling in large rivers where benthic fauna is otherwise inaccessible. Similar samplers have been described by Wene and Wickliffe (1940) and Dickson *et al*. (1971) for use in shallow streams. This sampling device was used in the Coeur d'Alene River in order to provide a clean, uniform substrate at all stations.

The baskets were filled with clean stones collected at each station and were placed on the stream bed parallel to the current in a shallow depression formed by removing surface cobbles. Two replicate baskets were placed at each station for four-week colonization periods. To remove the basket without loss of organisms, a screen-bottom pail was held immediately downstream from the basket, which was then lifted into the pail. It was found, however, that relatively few insects were dislodged during collection. The contents of the basket were emptied into a white enamel pan, and each stone was rinsed and checked for organisms and replaced in the basket or discarded. The organisms were preserved in 70% isopropyl alcohol for later examination.

In the Spokane River, multiple-plate artificial substrata similar to those described by Fuller (1971) were utilized to colonize and collect organisms after a period of 4-6 weeks. The same methods (and in most cases the same personnel) as those described above for the Coeur d'Alene River were used to collect the samples.

A short-term study also was conducted between July 31 and August 9, 1973 during low water flow. In this instance, a modified Hess sampler (Figure 19) was utilized (a cylindrical sampler 48 cm x 36cm dia with screen mesh of 1.2 mm). The sampler is placed in .5 to .75 m of water and anchored to the sediment. The rock and sediment within the confines of the sampler are removed, sieved (#30) and examined for organisms. The screen of the sampler then was examined for macrofauna. All specimens were preserved in 70% ethyl alcohol for transport to the laboratory. These samplers should not be confused with the Mundie sampler (Figure 20), which was used to determine the size of particulate in the Coeur d'Alene River and is described in a later section.

In the laboratory, the macroinvertebrate collections were sorted, identified and enumerated with the aid of an illuminated magnifying lens and binocular microscopes. Keys by Usinger (1968), Ward and Whipple (1963) and Mason (1968) were employed in making identifications. Following enumeration of taxa and individuals, the Shannon-Weaver diversity index,

$$d = -\Sigma n_i \ln n_i \quad \text{or} \quad D = -\Sigma \frac{n_i}{N} \log_2 \frac{n_i}{N}$$

was used to arrive at a diversity value for each sample. This index has been employed with increasing frequency as a quantitative measure of benthic community structure (Wilhm and Dorris, 1966, 1968; Dickson et al., 1971). Values of less than 1.5 generally indicate a polluted situation, while values greater than 3.0 indicate a healthy aquatic community. Values lying between these extremes are less readily definable and the community composition then should be examined for the presence or absence of pollution-sensitive species.

Periphyton Collection and Analysis--Coeur d'Alene River

The glass slide method of periphyton collection described by Butcher (1932) was employed in the Coeur d'Alene River. It is believed that the periphyton community colonizing this type of artificial substrate is only slightly different from the natural epilithic community (Sladecekova, 1962). The slides provide a standardized substrate between stations and have a known area of surface necessary for quantitative expression of cell counts.

Slide holders were devised by removing the covers and backs from wooden slide boxes and inserting a 30cm threaded metal rod through the center of the frame (Figure 21). Sixteen slides were placed in each frame and held in position with a flexible wire wrapped around the frame. Two frames were placed at each station by working the rod into the substrate so that the slide holder was in close proximity to the stream bed. The slides were parallel to the current. Replicate slides were recovered from each station after two- to five-week exposure periods and placed in 5% formalin for later examination.

Figure 18. Barbeque Basket: Ready for Placement in the Coeur d'Alene River.

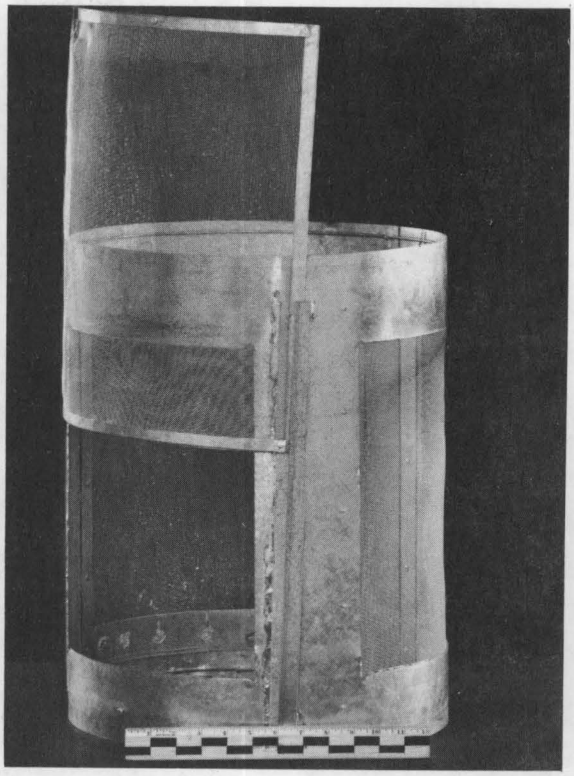

Figure 19. Modified Hess Sampler used for Obtaining Grab Samples in the Spokane River.

Figure 20. University of Idaho Investigator Operating Mundie Sampler.

Figure 21. Slide Holder Developed by University of Idaho Researchers for use in Coeur d'Alene River.

In the laboratory, the preserved samples were removed from the slides and examined microscopically for types and numbers of algae. Because of the extremely small size of most of the algal cells in the collections, a Palmer plankton counting cell (Palmer and Maloney, 1954) with a .1-ml capacity was used. The contents of the cell were examined under 250X magnification with the aid of a Whipple ocular micrometer. The entire area of the counting cell was scanned and types of algae present and their relative abundance were recorded. A strip count then was made, 25-50 fields being counted, and total cells per mm^2 of slide surface was calculated (APHA-Standard Methods, 1971).

Periphyton Collections and Analysis--Spokane River

Initially, periphyton collections from the Spokane River were by slide techniques similar to those described above; however, due to fluctuation of water levels (largely controlled by releases through the Post Falls Dam), this method proved unfeasible. A good portion of the time the slides were left dry or so deeply submerged that they could not be retrieved. This problem was solved partially by utilizing #7200 Easy Way Barbecue tumble baskets through which a 10cm length of 10mm (od) glass tubing was inserted. The tubing was fastened to a .64cm- (1/4-inch) diameter steel rod running through the skewer bracket on the basket (Figure 22). The glass tubing provided a surface attachment area of 31.4 cm^2. The baskets were secured along the stream bank by nylon cord. The method was highly successful, but unfortunately the attachment sites were hard to camouflage and led to losses by vandalism and the curiosity of cyclists, hikers and fishermen. Nameplates and work descriptions left at sites actually increased incidents of damage.

Periphyton samples were collected at 3-week intervals by simply drawing in the basket, retrieving the glass rod, inserting another and returning the basket. The glass rod or tubule was placed in 20 x 120mm screw-top bacterial culture tubes, dusted with $MgCO_3$ and stored under ice. At the WSU lab, a 10mm section was removed for identification and counting. The remainder was frozen to disrupt cell walls for later chlorophyll "a" analysis extraction and measurement by the Trichromatic Method for Chlorophyll as described in APHA-Standard Methods (1971). Spectrophotometric measurements were made with a Beckman DU-2 spectrophotometer utilizing a 2cm cuvette.

Plankton Collections and Analysis--Spokane River

Two 500ml water samples were collected at .5m depth at each station. One was taken for chlorophyll "a" determination and the other for qualitative and quantitative algal enumeration. Upon collection, the sample for chlorophyll "a" determination was treated with .1 g $MgCO_3$ to prevent pheophytin formation. These samples were processed within 6-8 hrs by filtration through $.80_\mu$ AAWG Millipore filters and frozen until extraction in 10 ml of aqueous acetone (90-10 percent acetone-water solution) and chlorophyll "a" determined by the Trichromatic Method as in the case of periphyton collections. The sample for algae enumeration was centrifuged at 15,000 rpm, the concentrate diluted to 10 ml, and a 1-ml subsample pipetted into a Sedgewick-Rafter cell for identification and counting under a microscope equipped with a Whipple disc. This method is similar to that described by APHA-Standard Methods (1971). Calibration was by the methods of Jackson and Williams (1962). Counts were expressed as cells/ml. Standard five-cell lengths of filamentous algal forms were counted as 1 unit/ml.

In situ ^{14}C phytoplankton production measurements were made as a valuable adjunct to the chlorophyll "a" measurements. They were made as consistent as convenience would allow. The methodology followed that outlined in APHA-Standard Methods (1971). Replicate 250ml light and dark bottles were filled with indigenous algae populations present in the river during sampling runs. Each bottle then was injected with a 5 microcurie/ml (μci/ml) solution of $NaH^{14}CO_3$ and suspended from flotation units (Figure 23) at levels of optimum photosynthetic intensities for diatom-green-algae populations (600-800 fc) (Rhyther, 1956a) for a period of 4-6 hours. After the incubation period a 50-100 ml subsample was filtered through .45μ filters by a field filtration system at .3 atmospheres pressure. The filter discs were attached to aluminum planchettes and counted in a Picker Magnachager 40 thin-window counter equipped with a Picker Spectroscaler IIIA. Milligrams carbon assimilated per m^3 were calculated using standard procedures (Vollenweider, 1969; APHA-Standard Methods, 1971).

Substrate Collection and Analysis--Coeur d'Alene River

In order to determine the size distribution of the substrate materials, the stream bed was sampled using the sampler and technique described by Mundie (1971). This sampler was developed for use in shallow streams and retains all particles, organic and inorganic, down to .05 mm in size (coarse silt). The sampler, operating on the principle of the Surber sampler, consisted of a box enclosing an area of stream bed of approximately .1 m^2 with an upstream opening which could be adjusted to regulate current inflow and two downstream nets, one inside the other, to retain fine materials dislodged during its operation (Figure 20).

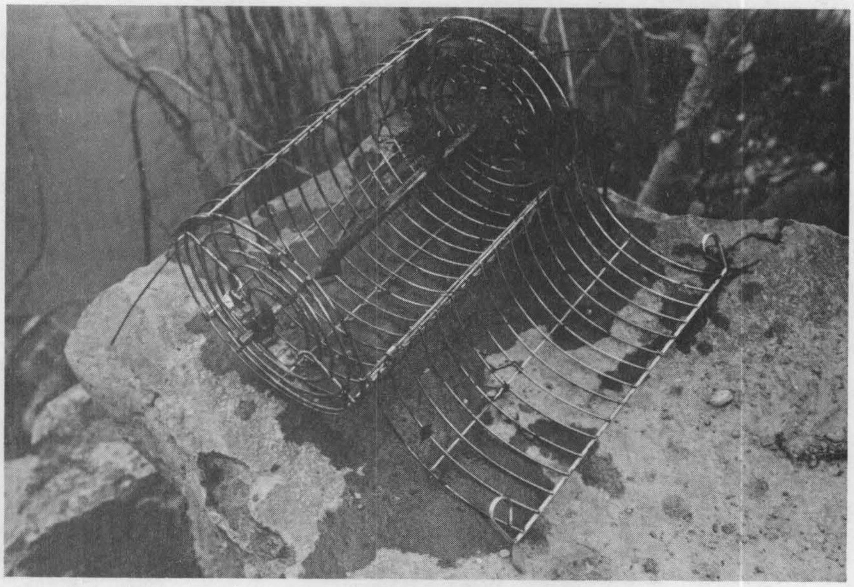

Figure 22. Barbeque Basket and Glass Rod Periphyton Apparatus Shown with Attached Growth.

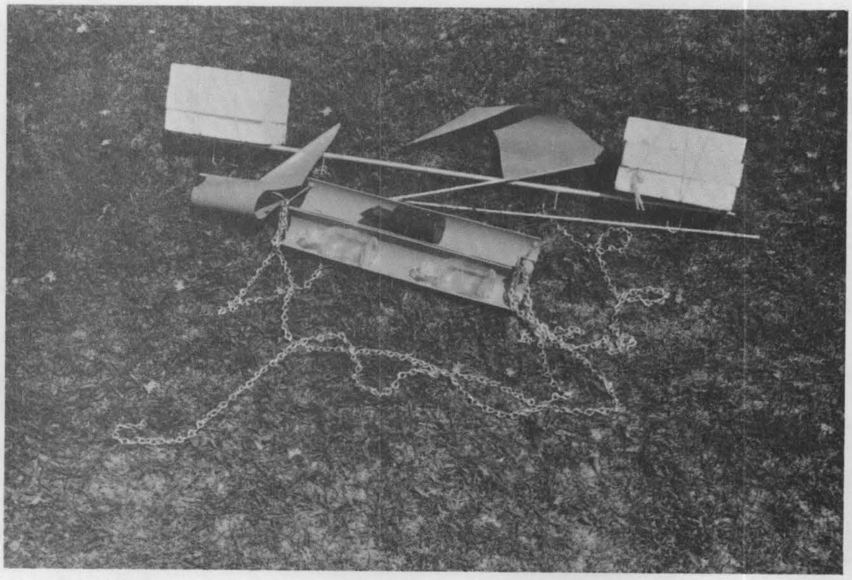

Figure 23. Float Used to Suspend Light and Dark ^{14}C Bottles During Incubation.

The nets employed included a standard 38-mesh Surber net nested inside a 270-mesh net having 53μ openings.

In practice, the materials enclosed by the box were scooped out to a depth of about 20 cm and placed in a pail while the current carried dislodged materials into the nets. The contents of the pail and nets then were placed in white enamel pans and the macroinvertebrates removed and preserved.

In the laboratory, the inorganic materials were oven-dried at 105 C and stones larger than 19 mm removed, sized and weighed. The remainder of the sample was sieved through a series of five Tyler screens using a mechanical shaker. The series included sizes 325, 170, 42, 9 and 3, corresponding to coarse silt, fine sand, coarse sand and fine and coarse gravel, according to Cummins' modification of the Wentworth scale (Cummins, 1962). Each size category then was weighed to the nearest tenth of a gram. Results were plotted as weight against size in order to determine the frequency distribution of particle sizes present in the sample (Royse, 1970). Size in mm was converted to phi units, which were defined by Krumbein (1934) as $-\log_2$ of particle diameter in mm. Use of this scale converts the unequal intervals of the Wentworth scale which represent a geometric progression to an arithmetic progression permitting plotting on equal-interval graph paper.

In order to determine whether significant amounts of silts or clays smaller than .05 mm were present in the substrate but lost to the Mundie sampler, control samples were collected immediately above water level where the surface was superficially similar to the in-current substrate. These samples were collected with a shovel and pail and subsequently analyzed in the same manner as the Mundie samples.

RESULTS AND DISCUSSION

I. Coeur d'Alene River

A. Water Quality

Physicochemical Conditions

The portion of the river covered in this phase of the study is shown in Figure 24.

Results of physical and chemical measurements of water quality parameters over the sampling season are presented in Figures 25-33 and Tables A-1 to A-3 in Appendix A. Little change from previous years was noted in any parameter measured. Parameters measured at the main stem stations showed the dilution effect of the mixing of the relatively unpolluted North Fork waters with the South Fork, which carries industrial and domestic waste materials. The concentration of dissolved materials increased as stream discharge diminished to low flow stage.

There was no significant difference in temperature among stations, and recorded levels were within acceptable limits for aquatic life. Oxygen levels represented daily maximums and were highest in the South Fork and main stem, probably responding to the photosynthetic activity of the abundant algal biomass at those stations (Table 4). The South Fork and main stem were slightly acidic, with a pH of less than 7.0 during most of the season (range 5.0-7.2). This may be the result of additions of acidic, industrial effluents to the soft, poorly buffered waters of this drainage (total alkalinity less than 20 mg/l). Turbidity was less than 50 mg/l at all stations. None of these parameters indicate serious water quality problems.

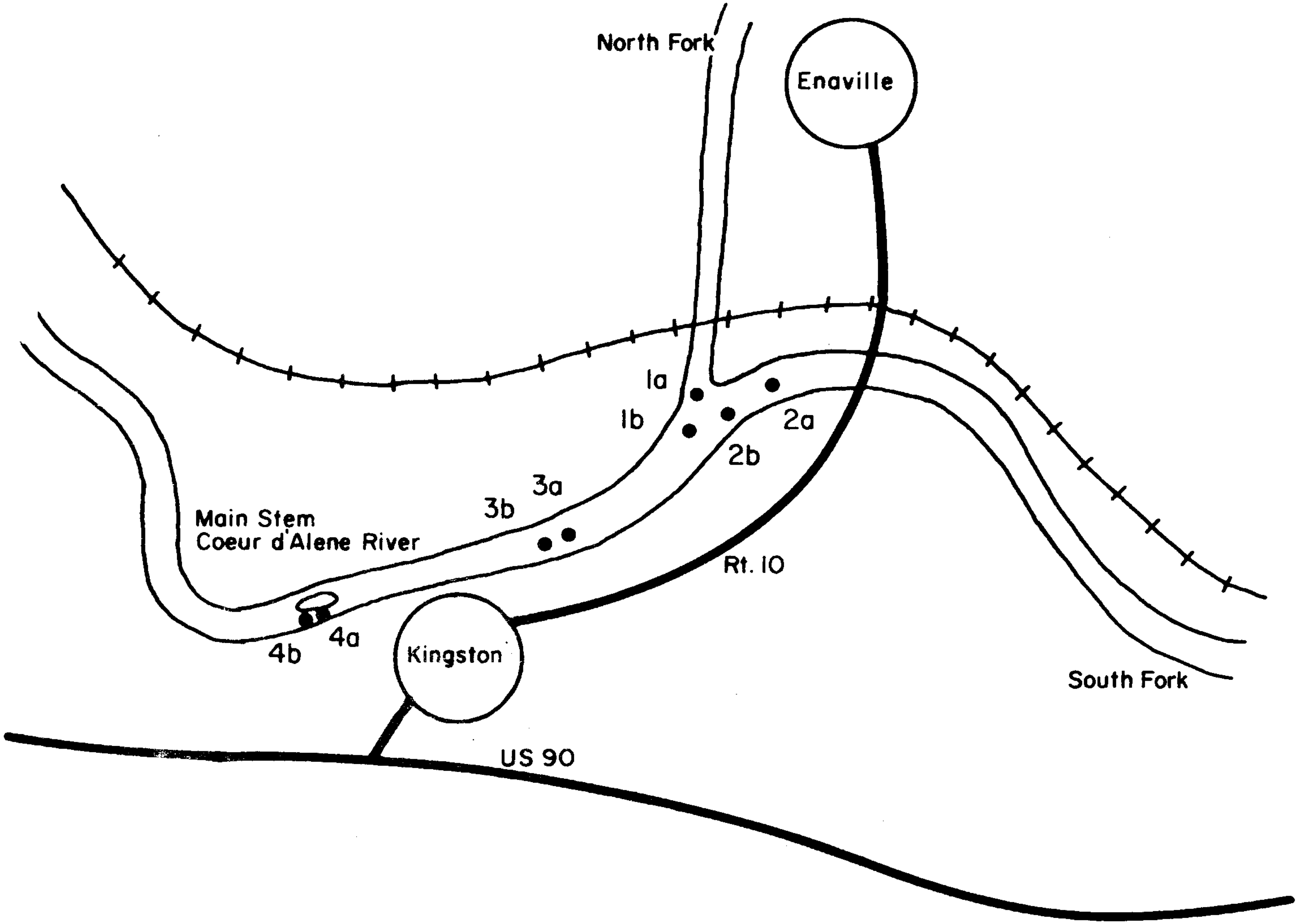

Figure 24. Coeur d'Alene River Study Area

Metallic Constituents Present in the Coeur d'Alene River

Examination of conductivity data indicates the presence of large amounts of dissolved ions originating in the South Fork drainage. These amounts were not considered to be excessive as far as upsetting the osmotic balance in aquatic organisms, but indicated a significant contribution of dissolved materials originating from mining and industrial effluents. The dissolved elements present in the river at concentrations which have been shown to be toxic to aquatic life included Zn, Cd, Pb and Fl.

Acute toxicity tests on the effects of heavy metals on salmonid fish have indicated an extreme sensitivity of these species to low levels of metal pollution. Sappington (1969) reported a 96-hour TL_m of .09 mg/1 Zn to cutthroat trout fingerlings in water from the North Fork of the Coeur d'Alene River. Zinc levels during this sampling period ranged from 5.5-23 mg/1 in the South Fork and 1.55-4.7 in the main stem. Rainbow trout placed in live boxes at several stations in the Coeur d'Alene River during the summer of 1973 all died within 48 hours (Bowler, 1974).

Studies on the effects of metals on aquatic macroinvertebrates have been limited, chiefly due to the difficulties of maintaining these organisms in the laboratory. In general, aquatic insects appear to be more tolerant to metals than are oligochaetes, crustaceans or molluscs (Klein, 1962). Jones (1940) found stoneflies, mayflies and midges living in water containing 60 mg/1 Zn. Newton (1944) reported a tolerance of water boatman, stoneflies and caddis flies to 500 mg/1 Zn. Bioassays conducted by Warnick and Bell (1969) demonstrated the tolerance to metals of three species of aquatic insects (Table 1).

Table 1. Bioassay Data on Three Species of Aquatic Insects (from Warnick and Bell, 1969).

Metal	Insect	96-hr TL_m mg/l	50% Survival	
			days	mg/l
Zn	*Acroneuria lycorias*		14	32
	Ephemerella subvaria		10	16
	Hydropsyche betteni		11	32
Cd	*A. lycorias*		14	32
	E. subvaria	2.0		
	H. betteni		10	32
Pb	*A. lycorias*		14	64
	E. subvaria		7	16
	H. betteni		7	32

Metal toxicity appears to be modified by several environmental factors. Toxicity increases with increase in temperature, decrease in dissolved oxygen and water hardness. In certain instances the effect of these factors may be antagonistic. Bartlett *et al.* (1974) found that combinations of Cu and Cd allowed for greater growth of *Selenastram capricornutum* than did equivalent doses of Cu. The salts of Ca and Mg, commonly present in natural waters, also have been shown to be antagonistic to the effects of Zn, Pb and Cu, reducing their toxicity to fish (Jones, 1938). Lloyd (1960) reported a 48-hour TL_m of 4.0 mg/l Zn at 320 mg/l alkalinity, 2.0 mg/l Zn at 50 mg/l alkalinity and .6 mg/l at 12 mg/l alkalinity for rainbow trout. Although natural alkalinity levels in the Coeur d'Alene River are reinforced by Ca, Mg and Na ions from mine effluents, these concentrations do not exceed 50 mg/l (Mink, 1971).

The presence of more than one heavy metal in solution may produce a synergistic effect, lowering the metal concentration at which toxic effects occur. Doudoroff and Katz (1953) found synergistic effects between the sulfates of Cu and Zn and Cu and Cd on salmonids. Sprague et al. (1965) state that mayflies are approximately equal to salmon in their sensitivity to Cu-Zn pollution but that caddis flies and some midges are at least 1.5 times more resistant.

Fluoride compounds, associated with phosphate rock, are present in the South Fork and main stem in concentrations above recommended limits of 1.5 mg/1 (Water Quality Criteria, 1968). Mink reported levels of 4 to 5 mg/1 Fl at the mouth of the South Fork and in the main stem below the confluence on August 6, 1970. On September 13, 1973, levels at these locations were 6.8 and 2.4 mg/1 Fl, respectively. Angelovic et al. (1961) reported TL_m values of 2.6-6.0 mg/1 Fl to trout in soft water.

Fluoride compounds have been compared favorably with arsenicals as insecticides while being considerably less toxic to mammals.

In contrast, Hemand and Warwick (1972) found tolerance to high levels of fluoride compounds in benthic estuarine organisms. In this case, salinity may have had an antagonistic effect on the fluoride toxicity.

Macronutrients Present in the Coeur d'Alene River Waters

Macronutrient concentrations were at moderate to high levels in polluted portions of the Coeur d'Alene River. Nitrate-nitrogen levels ranged from highs of .15 mg/1 in the North Fork to .34 mg/1 in the South Fork. Total phosphate concentrations were greater than 2.0 mg/1 in the South Fork from mid-August to late September while being less than .08 mg/1 in the North Fork. Phosphate compounds were derived from industrial as well as domestic waste effluents. High sulfate concentrations probably were derived from oxidation of sulfides in ores and tailings,

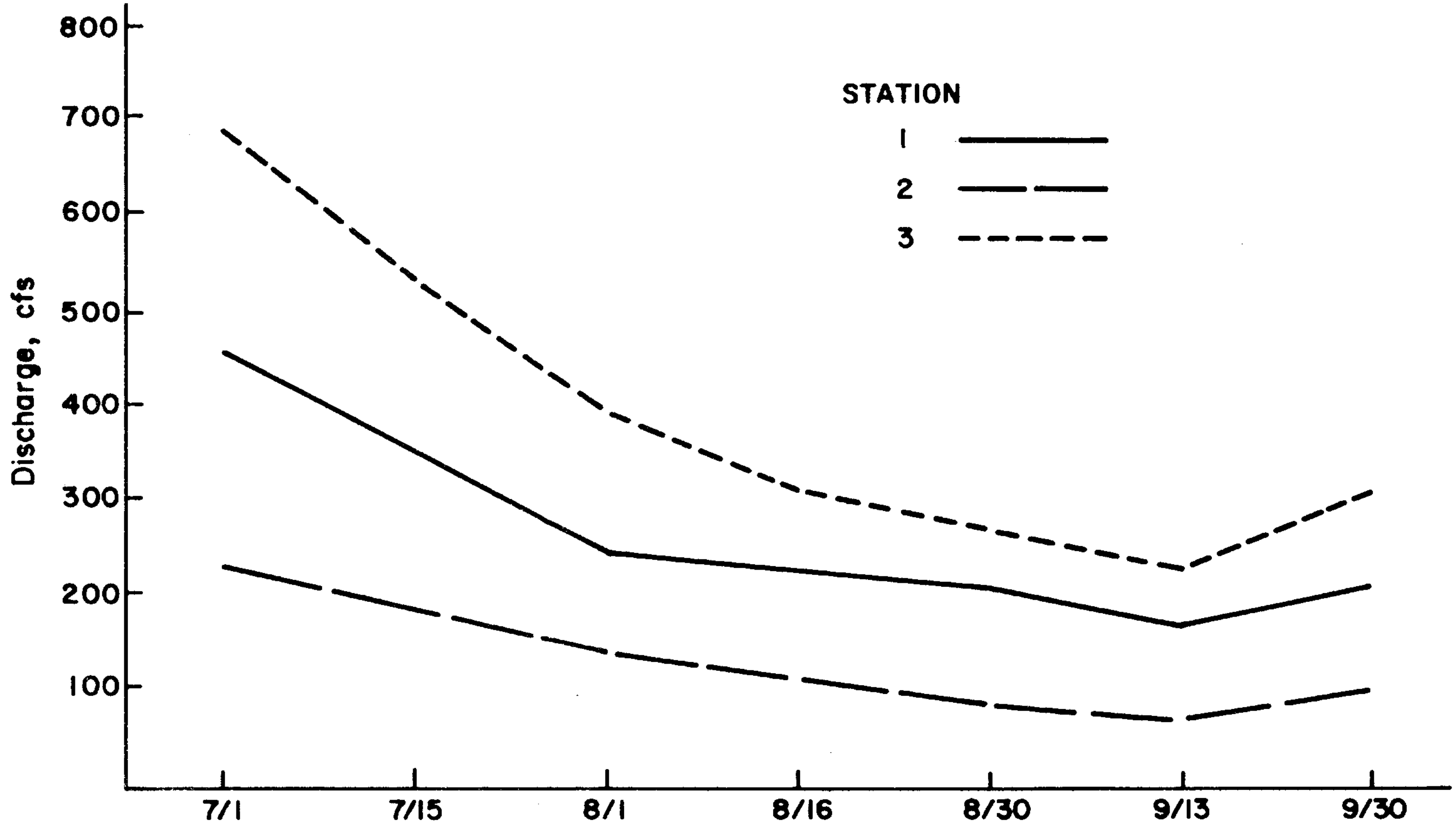

Figure 25. Coeur d'Alene River Flow, 1973.
(U.S. Geological Survey)

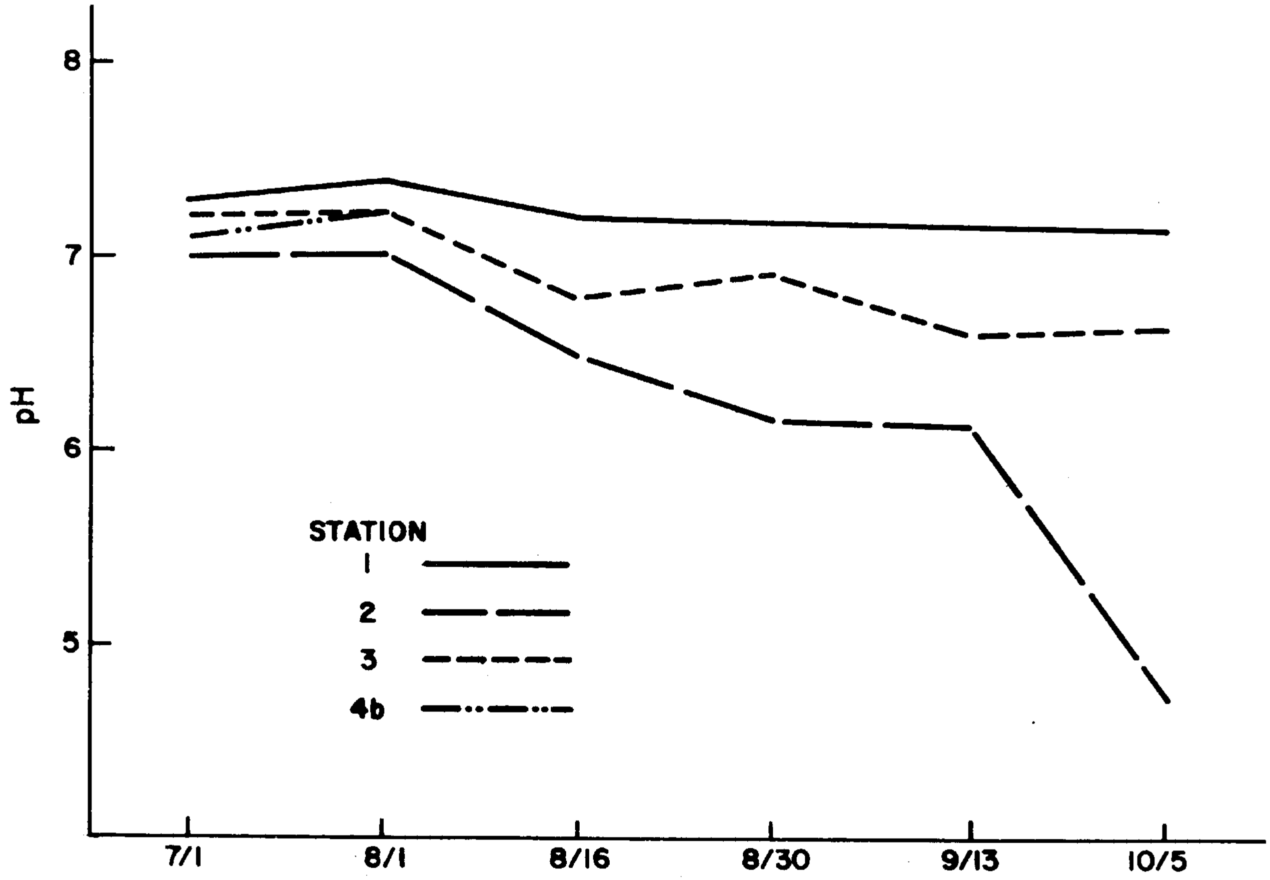

Figure 26. Measurement of pH, Coeur d'Alene River, 1973.

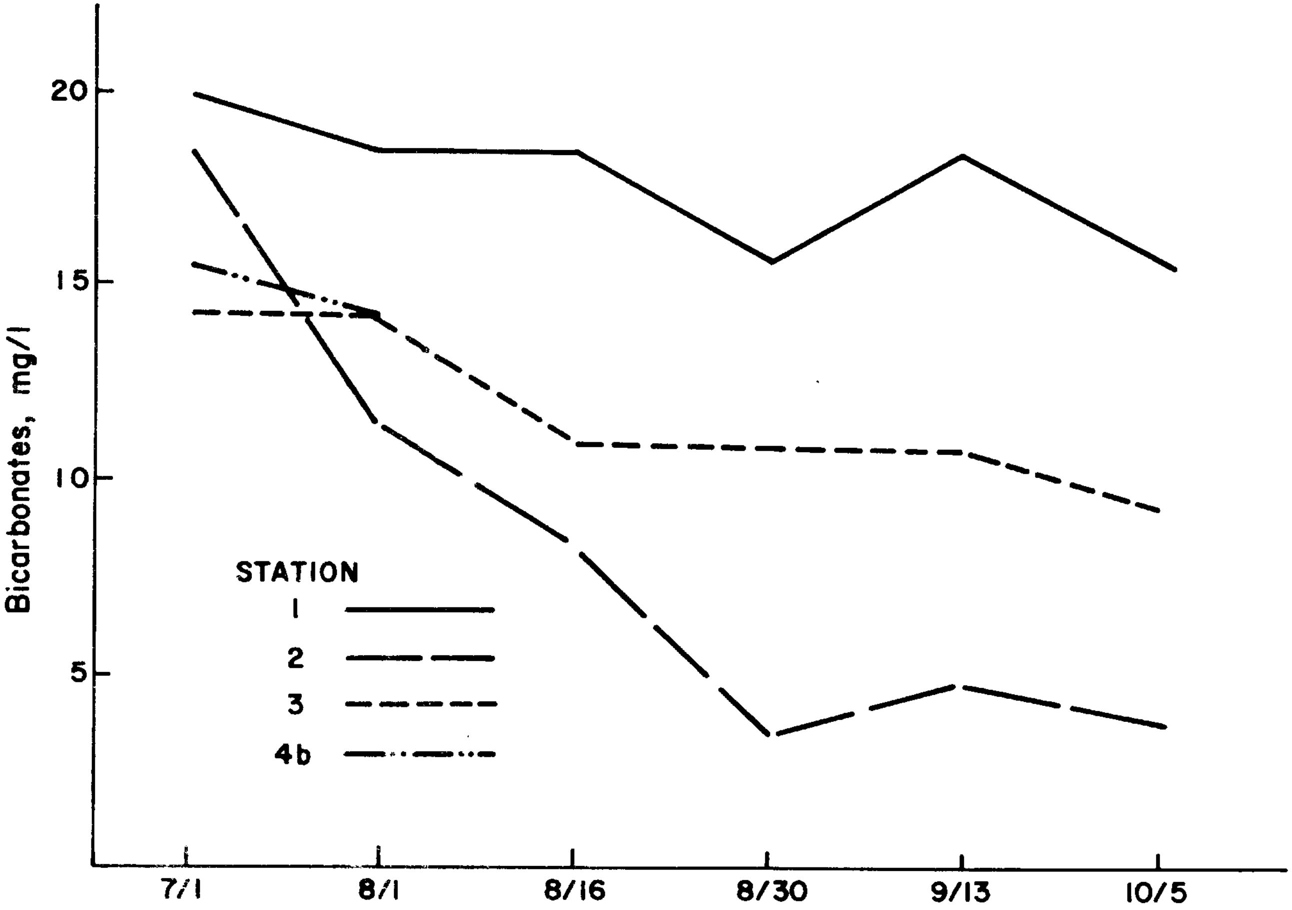

Figure 27. Bicarbonate Alkalinity Measurements, Coeur d'Alene River, 1973

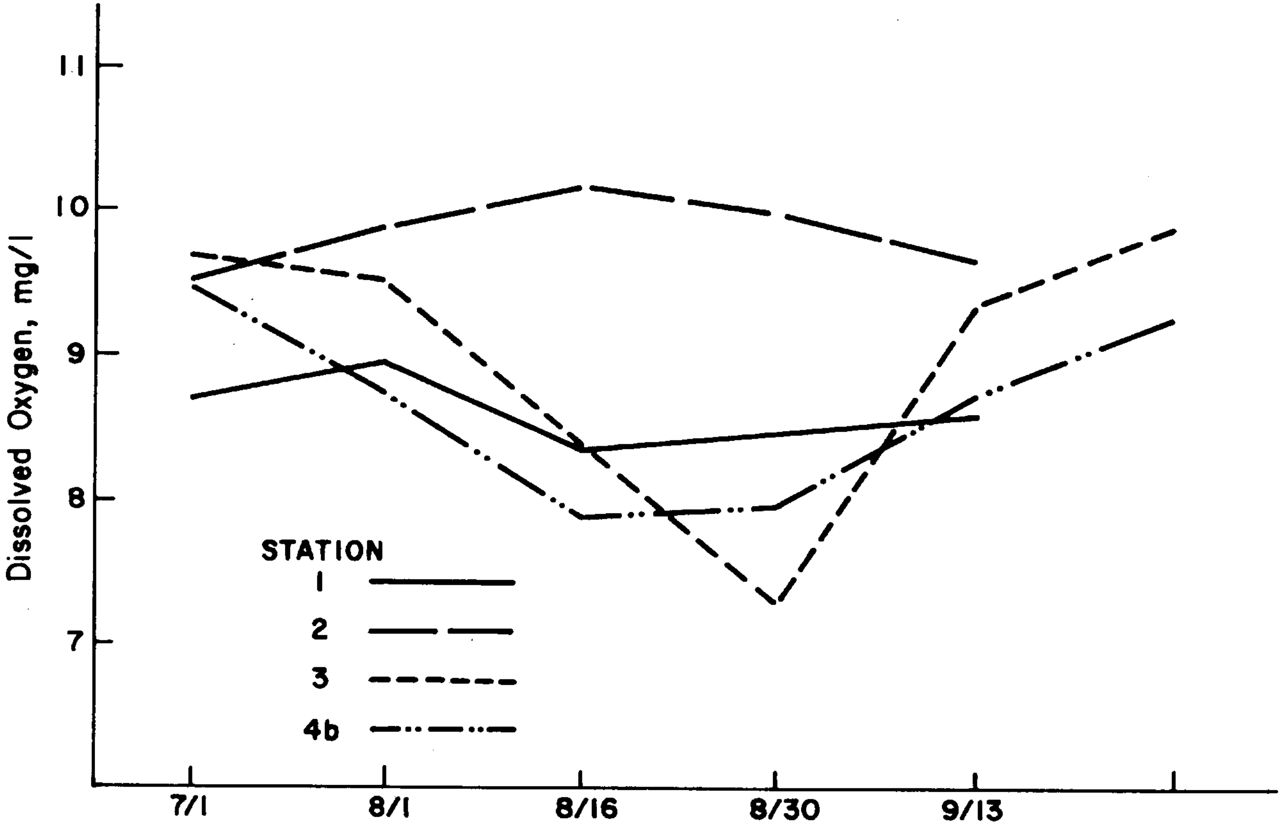

Figure 28. Dissolved Oxygen Measurements, Coeur d'Alene River, 1973.

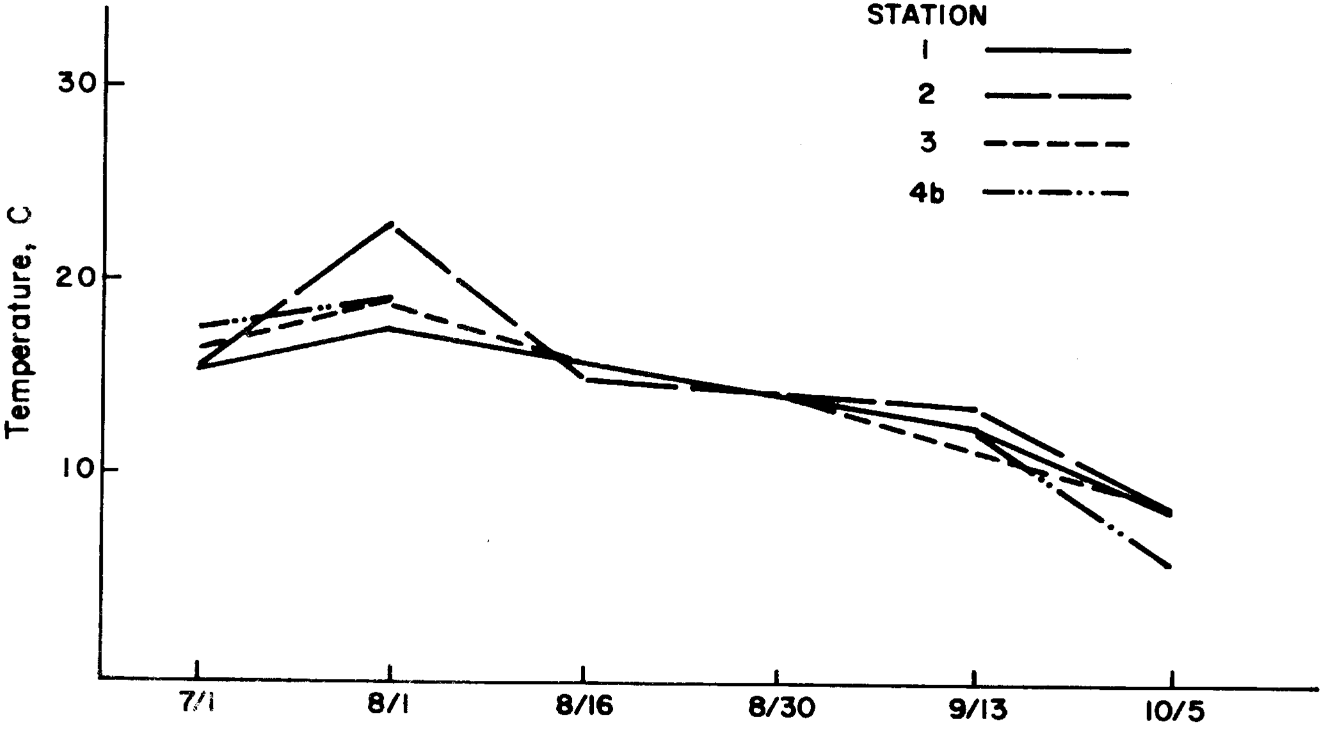

Figure 29. Water Temperature Measurements, Coeur d'Alene River, 1973

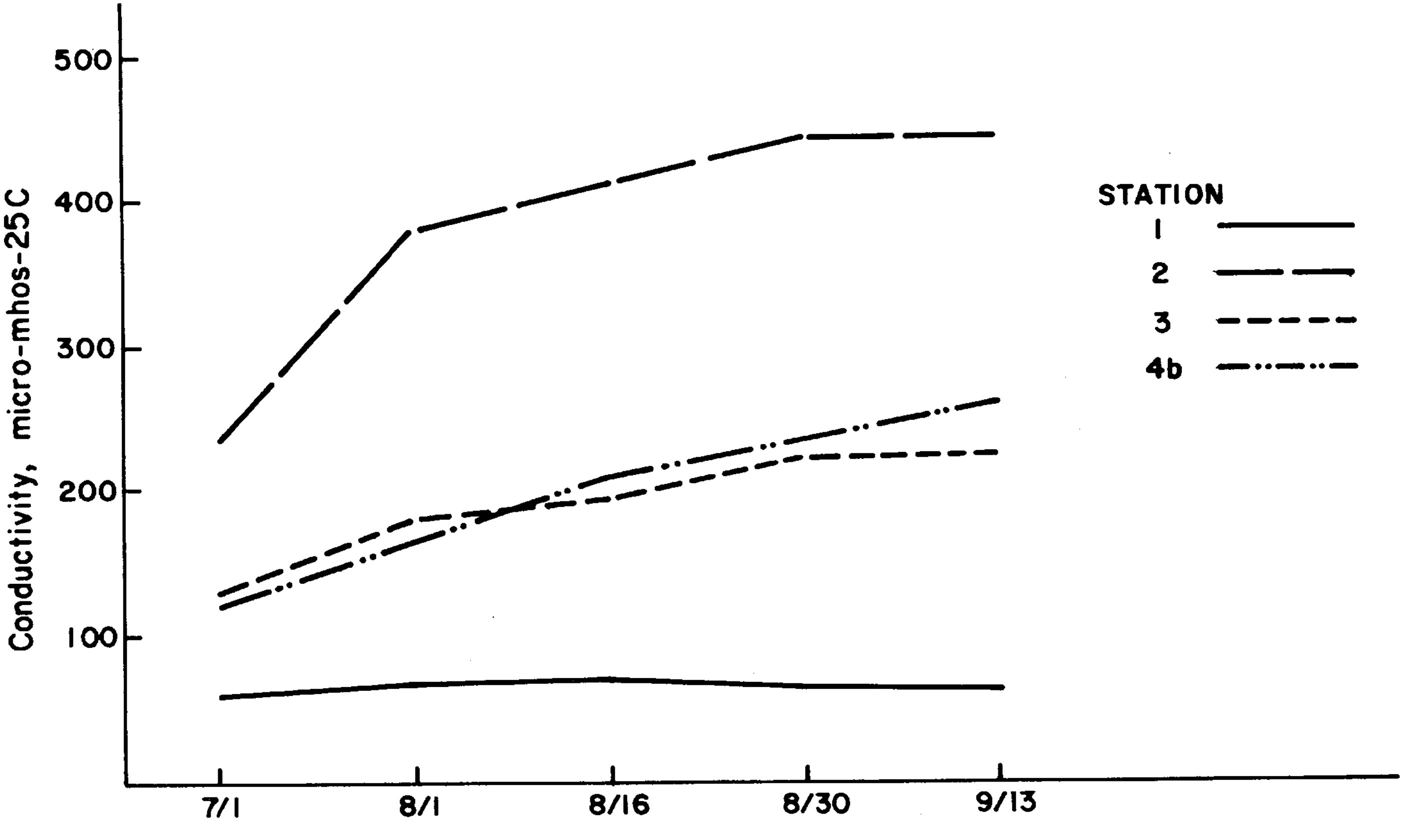

Figure 30. Conductivity Measurements, Coeur d'Alene River, 1973

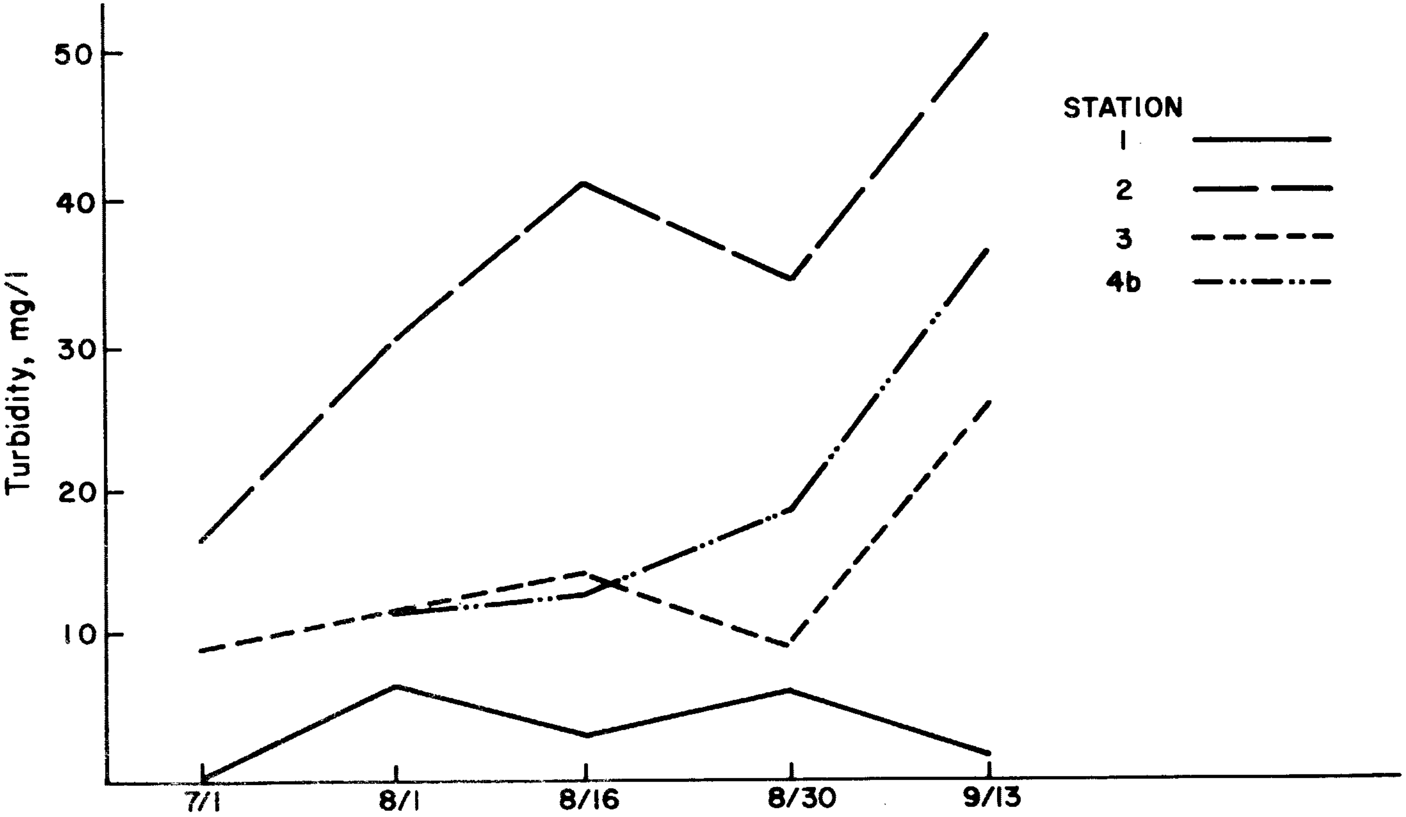

Figure 31. Turbidity Measurements, Coeur d'Alene River, 1973

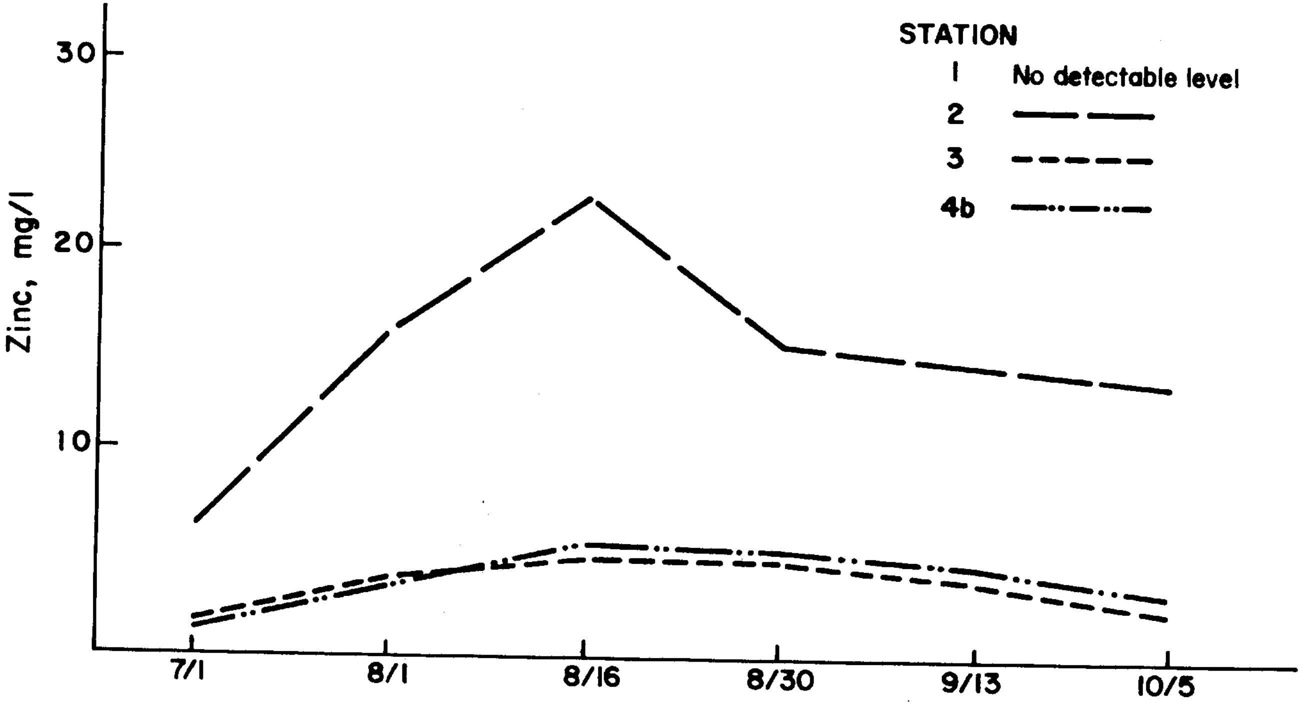

Figure 32. Zinc Measurements, Coeur d'Alene River, 1973

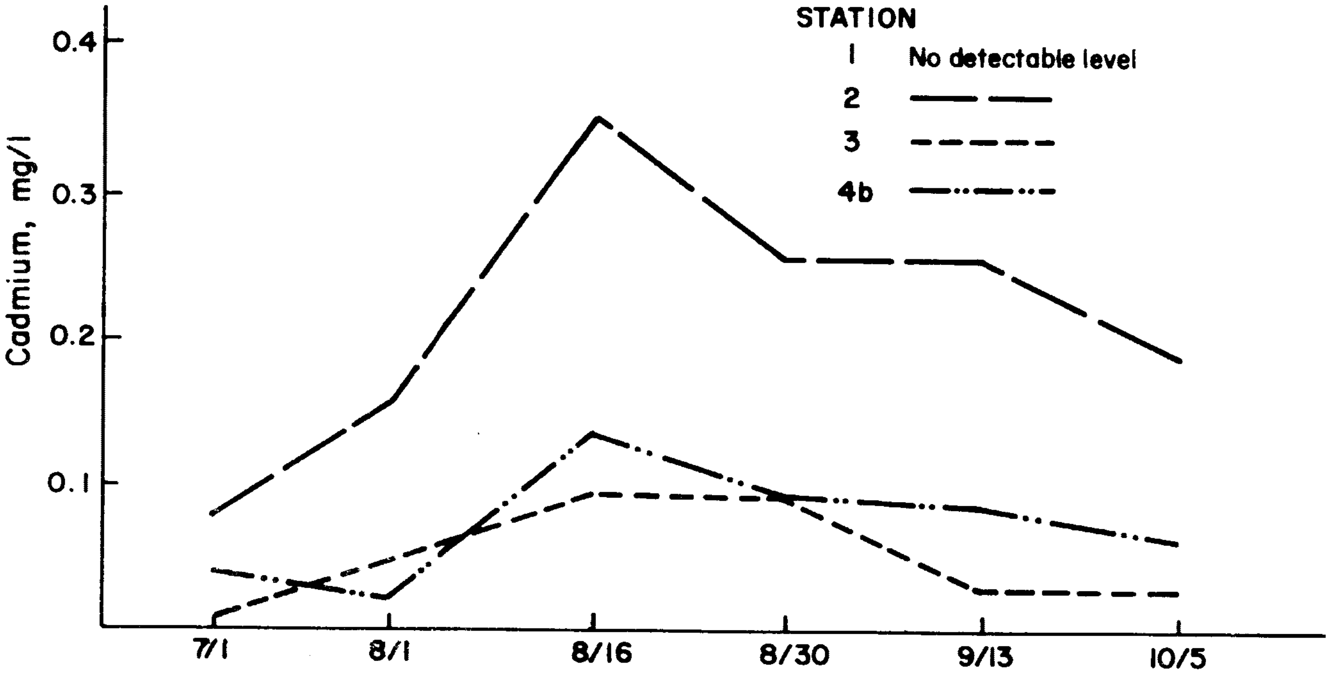

Figure 33. Cadmium Measurements, Coeur d'Alene River, 1973

although a small portion may have originated from mineralization of organic wastes. These high levels of nutrients stimulated the growth of algae to bloom proportions in the South Fork and main stem of the river during the period of study.

B. Benthic Algal Community

Dense growths of benthic algae have been observed in the South Fork and main stem of the Coeur d'Alene River during low-flow periods, since the decrease in silt load following settling pond containment of mine and mill fines (Savage and Rabe 1973). In order to make a quantitative and qualitative assessment of this flora, glass slides were established at five sites in the river on August 1, 1973. These sites included glide areas (smooth flowing water) at Stations 1b, 2a and 3b; a pool at 4a, and a riffle at 4b (Figures 1 and 24). Current velocity and water depth at these stations are listed in Table 2. Slides were collected weekly for five weeks following a preliminary two-week colonization period.

Table 2. Current Velocity in cm/sec and Water Depth (in cm) at Slide Locations, August 1-September 13, 1973.

Date	Glide			Pool	Riffle
	1b	2a	3b	4a	4b
8/1	52 (41)	36 (30)	70 (36)	nd[1] (46)	104 (25)
8/8	50 (38)	35 (43)	73 (38)	nd (43)	120 (15)
8/16	45 (43)	34 (38)	69 (33)	nd (43)	98 (15)
8/23	62 (41)	30 (33)	72 (33)	nd (43)	98 (20)
8/30	53 (41)	30 (38)	66 (36)	nd (43)	69 (15)
9/5	49 (36)	33 (41)	67 (36)	nd (43)	59 (13)
9/13	--	25 (41)	72 (31)	nd (43)	61 (15)
Mean	52 (40)	32 (38)	70 (35)	nd (43)	87 (17)

---

[1] No detectable current.

Qualitative Determination of Benthic Algae in the Coeur d'Alene River

Qualitative examination of the samples revealed that entirely different communities were present in the polluted and unpolluted portion of the river (Table 3). In the North Fork, an epilithic community of encrusting diatoms predominated on the slides and on the clean cobble substrate. In the South Fork and main stem, the fine inorganic and organic sediments deposited on the stream bed during low flow apparently supported an abundant epipelic flora. The algae cells comprising this community may be motile, loosely attached to sand grains or free-lying in the sediments (Round, 1965). A minute (4-7 μ), unicellular green alga, Chlorella, comprised over 95% of the South Fork community, while the main stem showed the effects of mixing of the two currents. Here, although Chlorella predominated, diatoms made up approximately 30% of the community. Filamentous greens and blue-greens were almost entirely absent during this sampling period. Oscillatoria sp. appeared in the main stem in low numbers early in September.

Table 3. Composition and Distribution of the Predominant Algal Types Among Stations in the Coeur d'Alene River Between August 8 and September 13, 1973.

Station	1b	2a	3b	4a	4b
Chlorophyta					
Chlorella	x[1]	xxx[3]	xxx	xxx	xxx
Scenedesmus	x	x	x	x	x
Filamentous form	x	x	x	x	x
Cyanophyta					
Oscillatoria			x	x	
Chrysophyta					
Diatoma	x	x	x	x	x
Synedra	x		x		x
Gomphonema	xx[2]		x	x	
Cocconeis	xx			x	
Fragillaria	xx			x	
Achnanthes	x			x	x
Cymbella	xx			x	
Melosira	x				
Centronella	x				

[1] x--present in low numbers
[2] xx--common
[3] xxx--abundant

Quantitative Determination of Benthic Algae in the Coeur d'Alene River

Total cell counts for each weekly interval are presented in Table 4. The weekly change in numbers is shown in Figure 34. The extremely high counts prevalent at Station 2a may reflect the high nutrient levels recorded at this station (Appendix Table A-1) as well as low current velocities. The epipelic community was undoubtedly underestimated in numbers by the sampling method employed. The difficulties inherent in quantitative sampling of the epipelic flora have been reviewed by Round (1953). This flora is easily disturbed by current fluctuations or turbulence, which may explain the roughly inverse relationship between

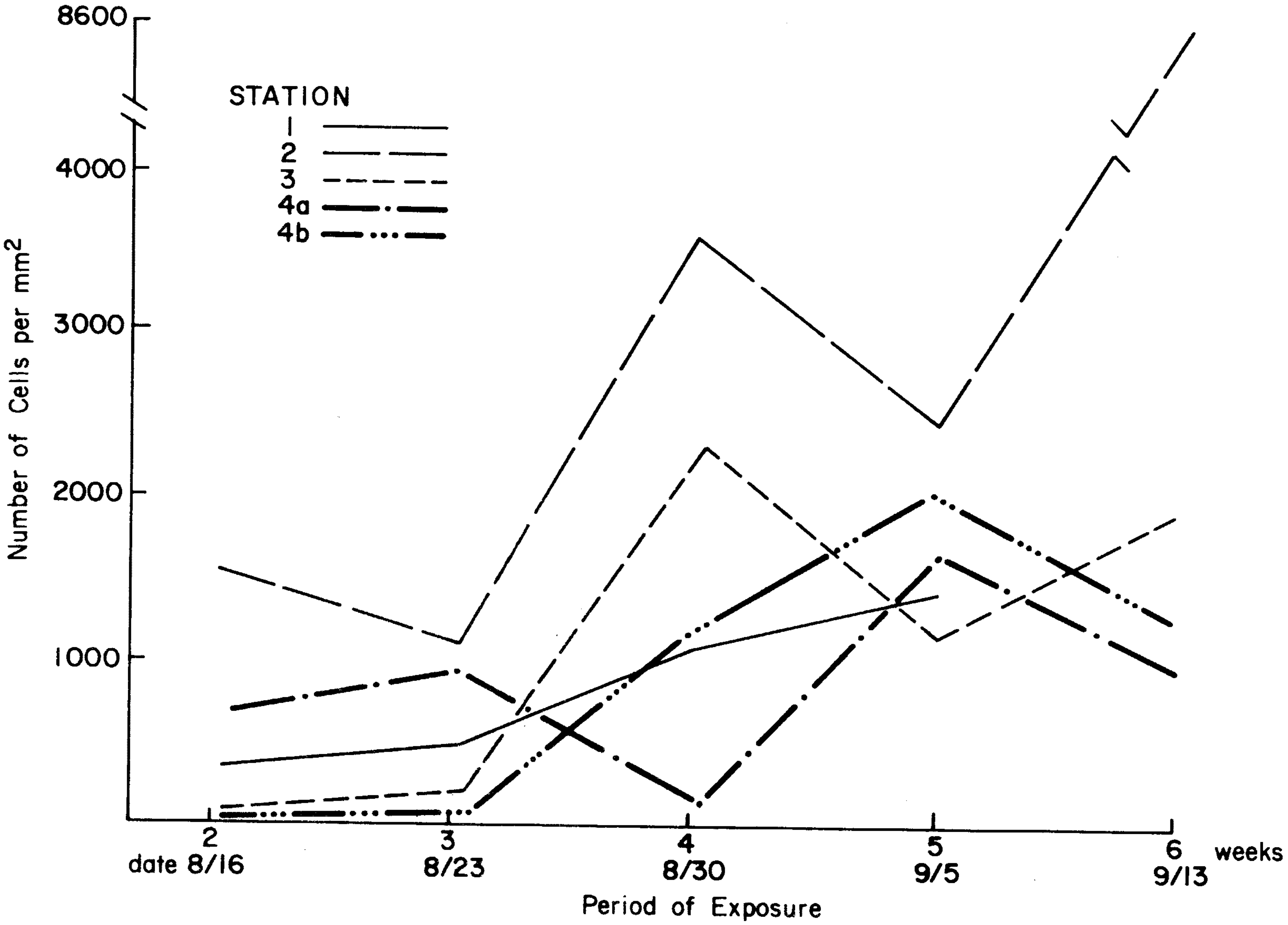

Figure 34. Weekly Change in Algal Cell Number on Glass Slides in the Coeur d'Alene River.

large changes in cell numbers and small changes in current velocity at Stations 2a, 3b and 4b, while changes in the pool samples (4a) may result from undetected eddies (Figure 35). The attached diatom community at Station 1b did not show these weekly fluctuations but increased gradually in numbers throughout the sampling period.

Table 4. Total cell counts (per mm^2) of Alga-Colonizing Glass Slides at Five Stations in the Coeur d'Alene River Over a Five-Week Period.

	Date Collected and Exposure Period				
Station	8/16/73 2 Weeks	8/22/73 3 Weeks	8/30/73 4 Weeks	9/5/73 5 Weeks	9/13/73 6 Weeks
1b	340	499	1162	1515	--
2a	1631	1141	3777	2550	8553
3b	72	201	2303	1234	1905
4a	749	984	146	1699	986
4b	66	36	1281	1875	1302

The density of the algal community at Station 4b was comparable to that at Station 1b although different in composition. This indicates that algal density per se was not inhibiting to benthic fauna, at least at Station 4b.

The predominance of one species at Station 2 may be due to either toxicity of the South Fork waters to other forms, or possibly an antibiotic effect of the dominant species. Algae exhibit varying degrees of tolerance to metals (Klein, 1962). Bartlett _et al_. (1974) demonstrated growth inhibition of _Selenastrum capricornutum_ exposed to less than .1 mg/l of Zn, Cd and Cu. Bioassays on the effects of Zn on _Nitzschia linearis_ and _Navicula seminulum_ indicated that both were inhibited by approximately 4 mg/l Zn in soft water (Water Quality Criteria, 1968).

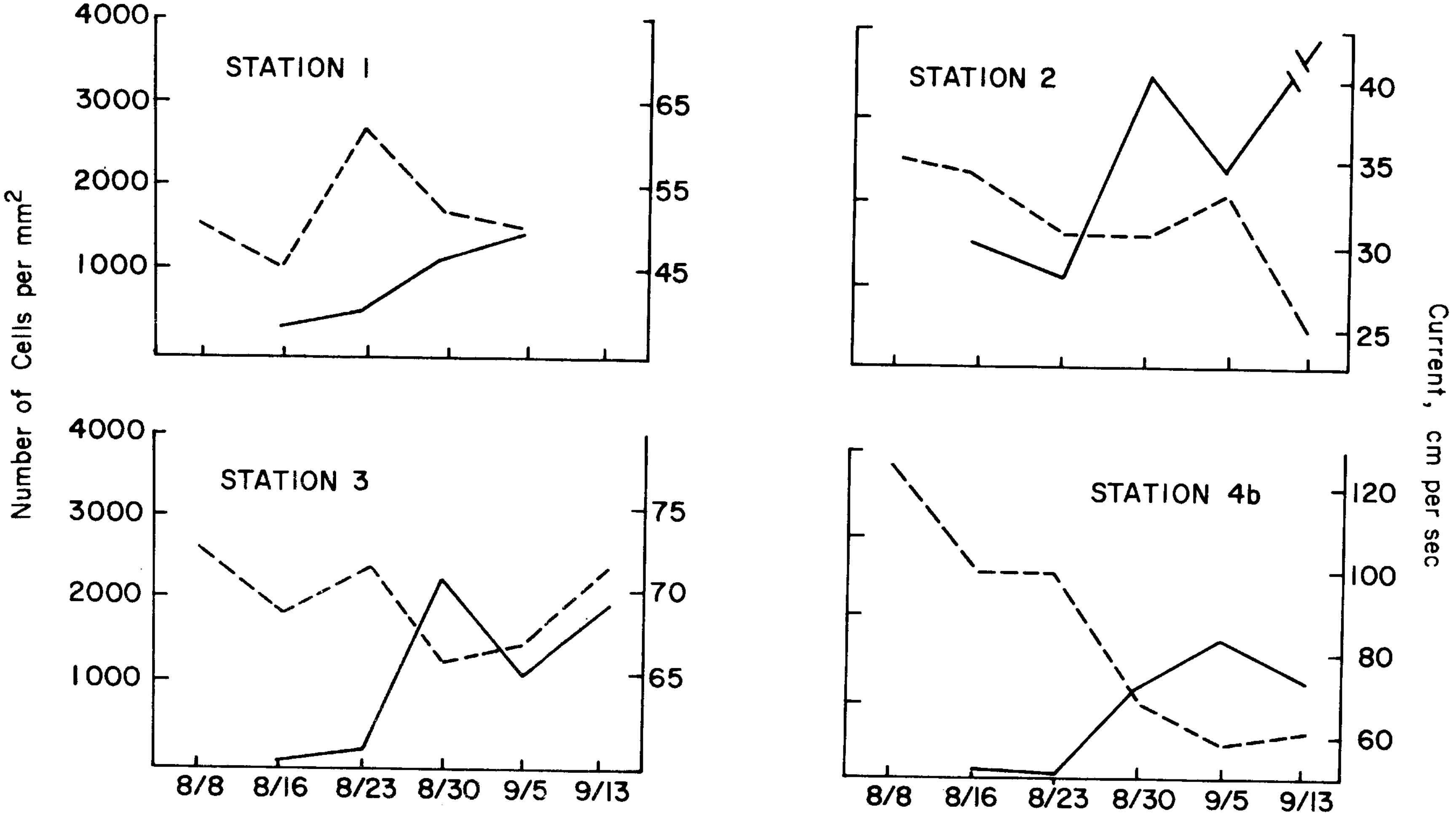

Figure 35. Periphytic Algae Cell Cell Counts (——) and Current Velocity (----) in the Coeur d'Alene River, August 8 Through September 13, 1973.

Palmer (1957) reported that .25 mg/1 Zn controlled all diatoms, 43% of the blue-greens and 18% of the green algae tested. Maloney and Palmer (1956) reported that .5 mg/1 Cu produced death in 57% of blue-greens, 35% of greens and 100% of diatoms tested. However, many forms do not seem to be greatly restricted, at least by moderate amounts of metals, when other environmental factors are optimum (Gale *et al*., 1973; Jones, 1940). Hassell (1962) demonstrated tolerance of *Chlorella vulgaris* to 250 mg/1 Cu.

The inhibitory effect of metabolites of some algae, including species of *Chlorella*, on associated species has been demonstrated in the laboratory (Proctor, 1957; Hartman, 1960; Prescott, 1960). Whether or not this effect prevails over other environmental factors in a stream is difficult to appraise.

C. Substrate Conditions

The hyporheal biotope is a vital component of the benthic faunal habitat. Coleman and Hynes (1970) and Bishop (1973) have demonstrated the presence of benthic organisms at all levels down to depths of 30 and 40 cm respectively in stream gravels. Various investigators have documented the deleterious effect of siltation on the normal benthic fauna of a gravel stream. Tarzwell (1938) found that silt and sand were poor in food materials. Tebo (1955) attributed low faunal production to the unstable nature of the fine sediments as well as to their low fertility. Fisheries biologists have correlated oxygen levels with available interstitial space in permeability studies of spawning gravels. McNeil and Ahnell (1964) state that spawning gravels containing more than 15% fines (inorganic particles less than .083 mm in diameter) are unsuitable for fry development due to inadequate oxygen levels.

Recent studies on benthic faunal distribution incorporating particle size analysis of stream bed materials have demonstrated the correlation between particle size distribution and benthos composition (Erikson, 1968; Cummins and Lauff 1969). Cummins observed varying ranges of tolerance and preference for particle size in nine species of stream insects. All groups avoided particles smaller than 1 mm and most were limited to materials coarser than 2 mm. All avoided silted areas and sought coarser sediments when siltation was present.

Tailings impoundment in the South Fork valley in 1969 resulted in a measurable decrease in suspended solids (Savage and Rabe 1973) and an observable reduction in fine silt deposits covering the gravel substrate in the South Fork and main stem. This study attempted to determine the amount of fines retained within the substrate and to describe the particle size distribution at all stations.

The substrate sampler utilized was developed by Mundie (1971) for use in shallow riffles and retains all particles down to .05 mm in size (coarse silt). The insect fauna and organic detritus as well as the inorganic bed materials may be collected by this method. In order to determine whether significant amounts of silts finer than the limits of the sampler were being lost during in-current sampling, control samples were collected at the stream edge immediately above water level.

Particle size categories are listed in Table 5. Weight and percent occurrence of each size class from in-current Coeur d'Alene River stations are listed in Table 6, while frequency distribution curves illustrate the distribution of particles among size classes (Figure 36). The highest percentage of particles was in the 19-50.8 mm size class (coarse gravel). The percentage of particles smaller than 1 mm was less than 10% at all stations. The Station 3 curve was bimodal, indicating a higher percentage of sands at this station. The low numbers of macroinvertebrates in the Surber samples as compared to the baskets at this station may reflect the sediment compaction suggested by this distribution (Tables 9, 10, 11 and 12).

The control samples contained a slightly higher percentage of sands than the in-current samples, as would be expected in a depositional environment (Figure 37). However, the amount of materials smaller than .05 mm was negligible--1.11, .44, .36 and 1.12% at Stations 1b, 2a, 3a and 4b, respectively (Table 6).

Benthic invertebrates collected from the Mundie samples are listed in Appendix A, Table A-2. Although smaller organisms such as Chironomidae larvae may have been overlooked in the field examination, these samples are similar in composition and structure to the Surber samples collected on October 5 (Tables 9, 10 and Appendix Table A-3).

No attempt was made to determine organic detrital content of the samples following mechanical analysis, as this process would have entailed ashing of large volumes of gravels. Small amounts of organic matter which appeared to be periphyton residue were observed in the finer sieves for all samples.

Table 5. Sediment Particle Size Classes.

Phi		Wentworth	NRC	Cummins	Tyler	Coeur d'Alene River Study		
φ	mm	1922	1957	1969	Sieve #	Tyler Sieve #	mm	Phi φ
-12								
-11		Boulder	Boulders	Boulder				
-10		gravel						
-9								
-8	256						88.9	-6.48
-7	128	Cobble	L cobbles	Cobble			64.0	-6.0
-6	64	gravel	S cobbles				50.8	-5.67
-5	32		VC gravel	Pebble			19.0	-4.25
-4	16	Pebble	C gravel					
-3	8	gravel	M gravel		2½	3	6.6	-3.67
-2	4		F gravel	Gravel	5			
-1	2	Granule	VF gravel		9	9	2.0	-1.00
0	1	VC sand	VC sand	VC sand	16			
+1	0.5	C sand	C sand	C sand	32	40	0.354	+1.50
+2	0.25	M sand	M sand	M sand	60			
+3	0.125	F sand	F sand	F sand	115	170	0.088	+3.50
+4	0.063	VF sand	VF sand	VF sand	250			
+5	0.032	C silt	C silt	C silt		325	0.044	+4.50
+6	0.016	M silt	M silt	M silt				
+7	0.008	F silt	F silt	F silt				
+8	0.004	VF silt	VF silt	VF silt				
+9								
+10								
+11		Clay	Clay	Clay				
+12								

Table 6. Frequency Distribution of Grain Size Measurements[1] from Four Stations in the Coeur d'Alene River, September 30, 1973.

Class Interval		Midpoint		Station							
				1a		2b		3a		4b	
mm	ϕ	mm	ϕ	gms	%	gms	%	gms	%	gms	%
0.04				21.8	0.11	13.6	0.07	1.2	0.01	9.1	0.05
0.04-0.08	+4.5 -+3.5	0.06	+4.00	22.0	0.11	22.7	0.12	2.6	0.02	13.6	0.08
0.08-0.35	+3.5 -+1.5	0.22	+2.50	236.6	1.20	190.9	1.02	35.0	0.22	104.6	0.59
0.35-1.98	+1.5 --1.0	1.17	+0.25	738.8	3.75	522.7	2.80	1192.9	7.59	700.0	3.93
1.98-6.68	-1.0 --2.72	4.70	-1.85	2533.7	12.87	1209.1	6.50	3845.5	24.47	2177.3	12.23
6.68-19.0	-2.72--4.25	12.84	-3.48	3698.6	18.78	3554.6	19.12	3445.9	21.93	3786.4	21.28
19.00-50.8	-4.25--5.67	34.90	-4.96	5656.7	28.72	9750.1	52.46	4885.0	31.09	7922.8	44.52
50.80-64.0	-5.67--6.0	57.40	-5.86	3376.8	17.15	3322.8	17.88	560.8	3.57	3081.9	17.32
64.00-88.9	-6.00--6.48	76.45	-6.24	-	-	-	-	1742.5	11.09	-	-
88.9				3408.5	17.31	-	-	-	-	-	-
Total weight				19693.5		18586.5		15711.4		17795.6	

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[1] After the method of Griffiths, 1967.

Table 7. Frequency Distribution of Grain Size Measurements from Streamside Control Stations, September 30, 1973.

Class Interval		Midpoint		Station							
				1a		2b		3a		4b	
mm	ϕ	mm	ϕ	gms	%	gms	%	gms	%	gms	%
0.04				104.3	0.44	226.6	1.11	60.5	0.36	172.2	1.12
0.04- 0.08	+4.5 -+3.5	0.06	+4.00	108.8	0.46	312.8	1.58	58.1	0.34	194.9	1.27
0.08- 0.35	+3.5 -+1.5	0.22	+2.50	747.9	3.15	1645.3	8.30	994.2	5.86	639.1	4.15
0.35- 1.98	+1.5 --1.0	1.17	+0.25	1115.0	4.70	4328.6	21.84	2107.2	12.41	707.1	4.59
1.98- 6.68	-1.0 --2.72	4.70	-1.85	2325.2	9.80	1835.7	9.26	2526.6	14.88	1151.3	7.48
6.68-19.00	-2.72--4.25	12.84	-3.48	3150.2	13.29	1935.4	9.76	3290.7	19.39	5547.9	36.04
19.00-50.80	-4.25--5.67	34.90	-4.96	3200.0	13.49	6005.7	30.30	2923.5	17.22	6554.1	42.58
50.80-64.00	-5.67--6.00	57.40	-5.86	4940.5	20.83	3530.1	17.81	1804.0	10.63	426.1	2.77
64.00-88.90	-6.00--6.48	76.45	-6.24	-	-	-	-	3209.1	18.91	-	-
88.9				8031.8	33.86	-	-	-	-	-	-
Total weight				19693.5		18586.5		15711.4		17795.6	

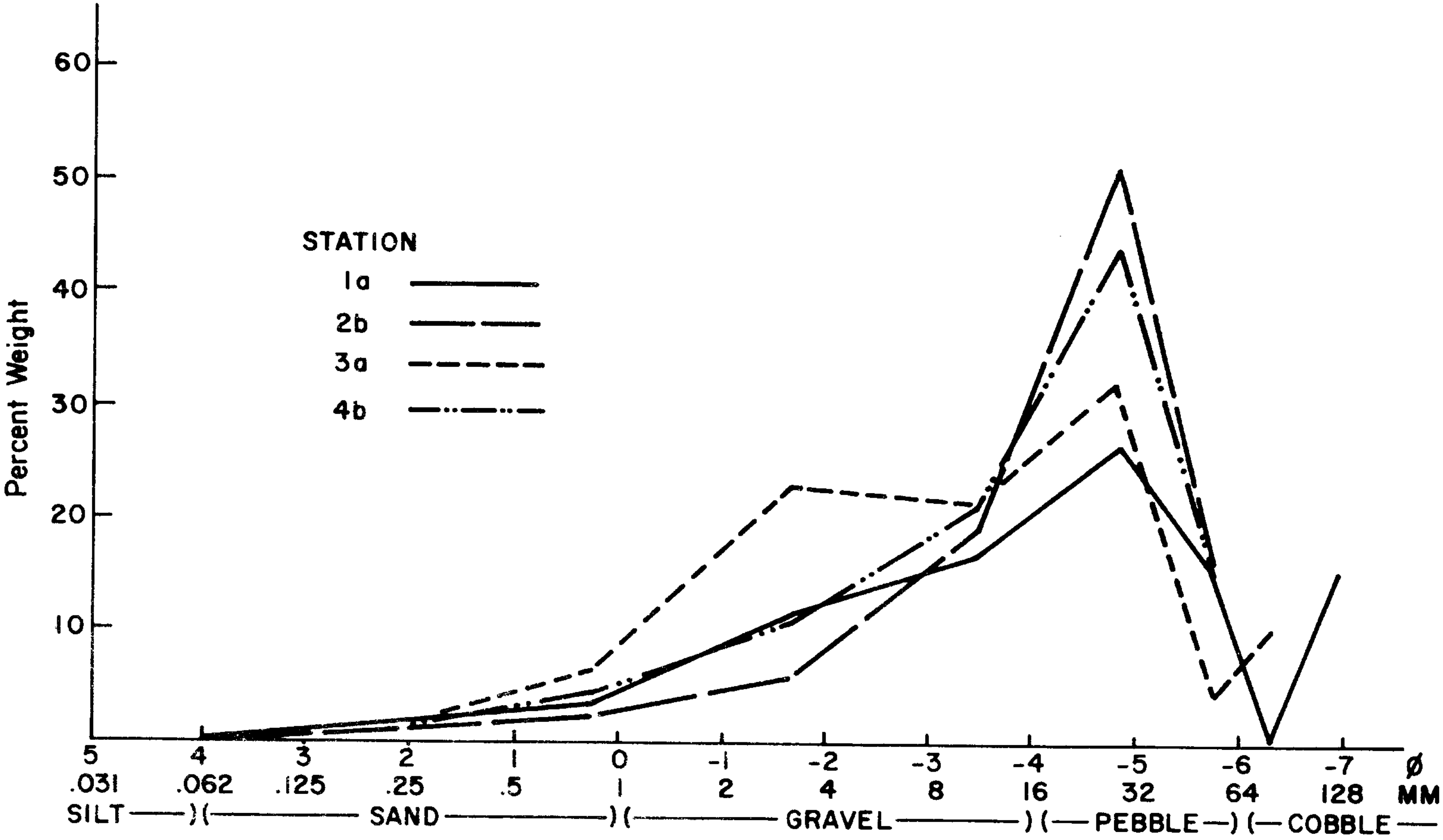

Figure 36. Frequency Distribution of Substrate Materials From Four Stations in the Coeur d'Alene River, September 30, 1973

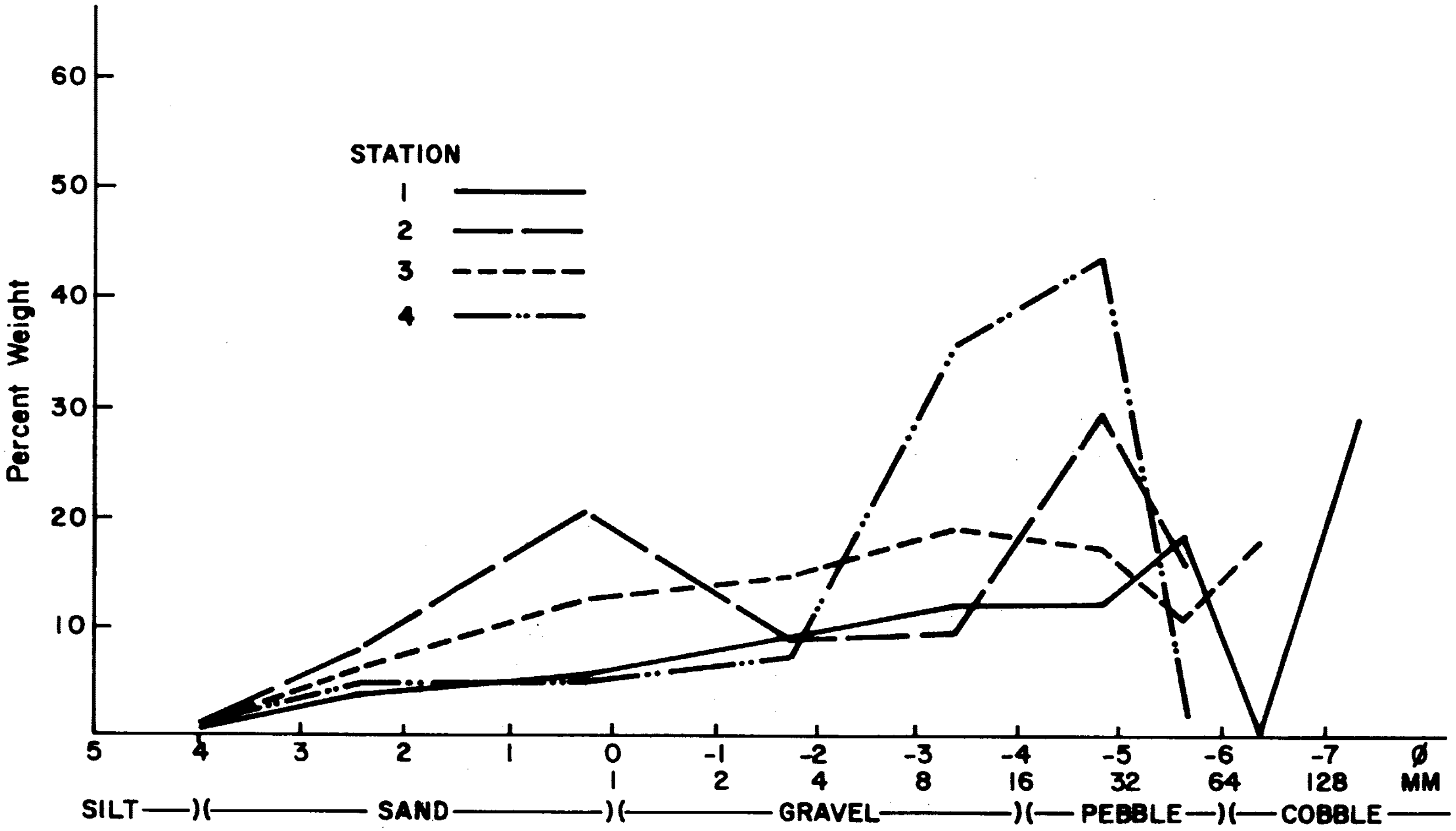

Figure 37. Frequency Distribution of Substrate Materials From Four Control Stations Located Above Water Level, September 30, 1973

D. Benthic Macroinvertebrate Community

Diversity Measurements of Macroinvertebrates in the Coeur d'Alene River

Reduction in mine tailings discharge to the South Fork of the Coeur d'Alene River in 1969 resulted in a limited recovery of the benthic macroinvertebrate community in previously unpopulated portions of the river (Savage and Rabe 1973). The density and diversity of the North Fork, South Fork and main stem communities from 1968 through 1971 are summarized in Table 8.

Table 8. Total Numbers (N), Number of Species (s) and Diversity (D) Typical of Macroinvertebrate Communities at Three Stations in the Coeur d'Alene River, 1968-1971. (Collections made in September. Sample size 0.2 m^2.)

Date		North Fork	South Fork (Smelterville)	Main Stem (Cataldo)
1968	N	738	-	250
	s	26	-	1
	D	3.329	-	0
1969	N	326	72	352
	s	27	1	3
	D	3.481	0	0.214
1970	N	770	276	624
	s	30	2	4
	D	3.356	0.03	0.192
1971	N	698	762	68
	s	25	4	2
	D	3.030	0.073	0.986

The predominant organisms in the South Fork and main stem were midge fly larvae and pupae (Chironomidae = Tendipedidae). These insects commonly have been observed in metal-polluted waters (Hynes, 1963). The insect next in abundance was the predaceous larva of the snipe fly, Atherix variegata. Adult riffle beetles also were present in the main stem. No significant improvement was noted in the benthic communities during the course of the above-mentioned study. Subsequent to decrease in silt load, a dense periphytic algal growth developed in polluted portions of the river during the summer season.

The Use of Artificial Substrata in an Attempt to Determine Colonization-Limiting Factors

During the present study, artificial substrates were provided for insect colonization in an attempt to determine whether the natural substrate conditions or the water chemistry was the primary factor limiting further recovery of the benthos. Although the difference in habitat prohibits absolute quantitative comparison between Surber and basket samples, it is apparent from the organisms collected (Appendix A, Tables A-3 and A-4) that the two communities were very similar at the North Fork station. Selectivity for Diptera (Chironomidae) and against Coleoptera in the baskets at this station resulted in some variation in frequency distribution of insect orders between the two types of samplers (Figures 38 and 39), accounting for lower diversity values in the baskets. Numerical abundance of insects in the baskets consistently exceeded that in the Surbers (Tables 9 and 10). The rapid recolonization of denuded areas in streams by drift organisms (Wene and Wickliffe, 1940; Waters, 1964) or by upward migration of hyporheal organisms (Bishop, 1973) as well as more space being available for colonization in the baskets may account for the greater density.

Whereas the North Fork supported an abundant and diverse benthic fauna, the insect community at the remaining stations clearly showed the

Table 9. Numbers and Percentage Composition of Macroinvertebrates in Basket Samplers in the Coeur d'Alene River.

		July 1-August 1		
		Station		
	1	2	3	4
Ephemeroptera	289 (9.6)	5 (2.3)	6 (1.5)	7 (1.1)
Plecoptera	62 (2.1)	-	8 (2.0)	2 (0.3)
Trichoptera				
Hydropsyche	936 (31.0)	-	81 (20.1)	-
Other	12 (0.4)	-	3 (0.8)	1 (0.2)
Coleoptera	41 (1.4)	43 (19.8)	57 (14.2)	5 (0.8)
Diptera				
Chironomidae	1474 (48.8)	167 (76.9)	173 (43.0)	626 (97.2)
Other	162 (5.4)	-	74 (18.4)	3 (0.5)
Miscellaneous	40 (1.3)	2 (0.9)	-	-
Total N	3016	217	402	644
Total species	32	8	17	12
		September 5-October 5		
Ephemeroptera	191 (32.1)	-	2 (2.6)	-
Plecoptera	33 (5.6)	-	2 (2.6)	-
Trichoptera				
Hydropsyche	165 (27.7)	-	7 (9.1)	11 (73.3)
Other	10 (1.7)	-	1 (1.3)	-
Coleoptera	16 (2.7)	1 (7.1)	1 (1.3)	-
Diptera				
Chironomidae	122 (20.5)	13 (92.8)	61 (79.2)	4 (26.7)
Other	55 (9.2)	-	3 (3.9)	-
Miscellaneous	3 (.5)	-	-	-
Total N	595	14	77	15
Total species	23	3	12	2

Table 10. Numbers and Percentage Composition of Macroinvertebrates in Surber Samples in the Coeur d'Alene River.

		July 1		
		Station		
	1	2	3	4
Ephemeroptera	18 (34.6)	-	1 (1.4)	8 (7.1)
Plecoptera	2 (3.9)	-	-	-
Trichoptera				
Hydropsyche	-	-	-	-
Other	2 (3.9)	-	-	-
Coleoptera	1 (1.9)	1 (14.3)	-	4 (3.5)
Diptera				
Chironomidae	27 (51.9)	6 (85.7)	73 (98.6)	99 (87.6)
Other	2 (3.9)	-	-	2 (1.8)
Miscellaneous	-	-	-	-
Total N	52	7	74	113
Total species	11	3	4	8
		August 1		
Ephemeroptera	80 (15.0)	3 (2.3)	-	9 (6.1)
Plecoptera	33 (6.2)	-	-	4 (2.7)
Trichoptera				
Hydropsyche	64 (12.0)	-	6 (16.7)	7 (4.8)
Other	54 (10.2)	-	-	-
Coleoptera	168 (31.6)	51 (39.5)	2 (5.6)	6 (4.1)
Diptera				
Chironomidae	92 (17.3)	67 (52.0)	26 (72.2)	119 (80.9)
Other	41 (7.7)	2 (1.6)	2 (5.6)	2 (1.4)
Miscellaneous	-	1 (0.8)	-	-
Total N	532	129	36	147
Total species	25	8	6	12
		October 5		
Ephemeroptera	55 (26.3)	-	-	-
Plecoptera	15 (7.2)	-	-	-
Trichoptera				
Hydropsyche	54 (25.8)	-	1 (14.3)	-
Other	5 (2.4)	-	-	-
Coleoptera	51 (24.4)	-	-	-
Diptera				
Chironomidae	15 (7.2)	8 (100)	6 (85.7)	1 (100)
Other	14 (6.7)	-	-	-
Miscellaneous	-	-	-	-
Total N	209	8	7	1
Total species	25	1	2	1

impact of adverse environmental conditions. The availability of an optimum substrate resulted in only slight differences between basket and Surber samples in the South Fork and main stem. The greatest difference occurred at Station 3, where basket samples consistently contained more species and numbers than the Surber samples. This station, located a short distance below the confluence, may have received a higher percentage of viable drift organisms than the lower main stem station (4b). At the same time, the natural substrate at Station 3 appeared to be more compact with a higher percentage of fines (Figure 36) than were present at the 4b riffle, where the swifter current prevented deposition of fines and the natural substrate provided a more suitable habitat for insects. In spite of an adequate substrate and the dilution effect of the North Fork current, however, the 4b community showed little improvement over the community present at Station 2 in the South Fork. The most successful species in the polluted portions of the river were Chironomidae, including representatives of the families Orthocladinae, Tanypodinae and Chironominae. Others observed in significant numbers were the net-spinning caddis flies, _Hydropsyche_ _sp_., _Atherix_ _variegata_, and two beetles, _Oreodytes_ _sp_. (Haliplidae) and _Brychius_ _sp_. (Dytiscidae).

Seasonal changes in community structure occurred at all stations (Table 11, Figures 40 and 41). In the North Fork these changes reflected normal life history rhythms such as hatching (_Ephemerella_ _serrata_), late instar increase in size and decrease in numbers (_Hydropsyche_ _sp_.) and emergence (_Baetis_ _tricaudatus_, Chironomidae). Species abundance and diversity showed little change. Changes in the South Fork and main stem communities were more pronounced, with almost complete elimination of all populations as the season progressed.

Table 11. Density and Diversity of Macroinvertebrates in Surber Samples.

Date		North Fork 1a	South Fork 2b	Main Stem 3a	 4b
July 1	N[1]	52	7	74	113
	s[2]	11	3	4	8
	D[3]	2.916	1.149	0.704	1.129
Aug. 1	N	532	129	36	147
	s	25	8	6	12
	D	3.460	1.937	2.096	2.129
Oct. 5	N	209	8	7	1
	s	25	1	2	1
	D	3.511	0	0.591	0

[1] N = Total number of individual organisms
[2] s = Number of species
[3] D = Species diversity

Table 12. Density and Diversity of Macroinvertebrates in Basket Samples.

Date		North Fork 1a	South Fork 2b	Main Stem 3a	 4b
Aug. 1	N[1]	1513	111	201	322
	s[2]	26	7	14	8
	D[3]	2.953	1.581	2.811	1.301
Oct. 5	N	303	11	39	7
	s	19	2	8	2
	D	2.739	0.694	2.068	0.782

[1] N = Total number of individual organisms
[2] s = Number of species
[3] D = Species diversity

In September, a test was designed to further separate substrate and water quality factors. Replicate baskets were placed in the North Fork and allowed to colonize for two weeks. At the end of this period, two baskets were removed and placed in the South Fork while a control basket was removed and replaced in the North Fork. After one day, the control basket and one South Fork basket were collected and after two weeks the second South Fork basket was collected. The results (Table 13) showed a pronounced reduction in insects over the exposure period in the South Fork.

Table 13. Community Structure in Control (North Fork) and Test (South Fork) Baskets in the Coeur d'Alene River.

Parameter	North Fork 1 day	South Fork 1 day	 2 weeks
N[1]	227	177	49
s[2]	18	13	4
D[3]	2.621	2.185	1.442

[1] N = Total number of individual organisms
[2] s = Number of species
[3] D = Species diversity

Species present after two weeks in the South Fork were two midges, *Hydropsyche sp.*, and a tipulid, *Antocha sp.*

A simultaneous test involved filling a basket with stones from the South Fork which were densely coated with the detrital materials and periphytic algae typical of that station. Comparison of the community structure in that basket after four weeks in the North Fork with a control basket indicated little difference in the two communities (Table 14).

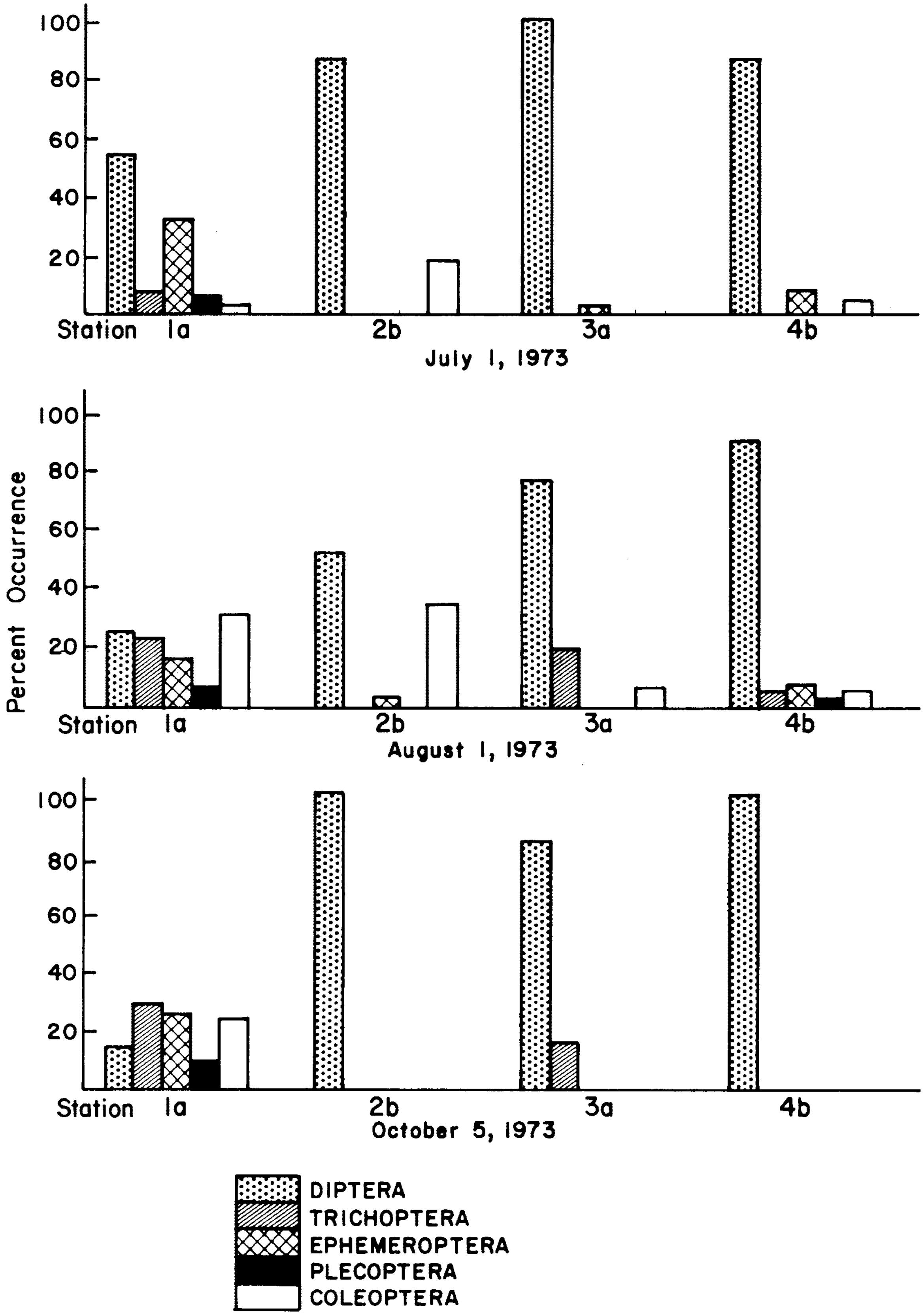

Figure 38. Percent Occurrence of Aquatic Insects by Order in Surber Samples

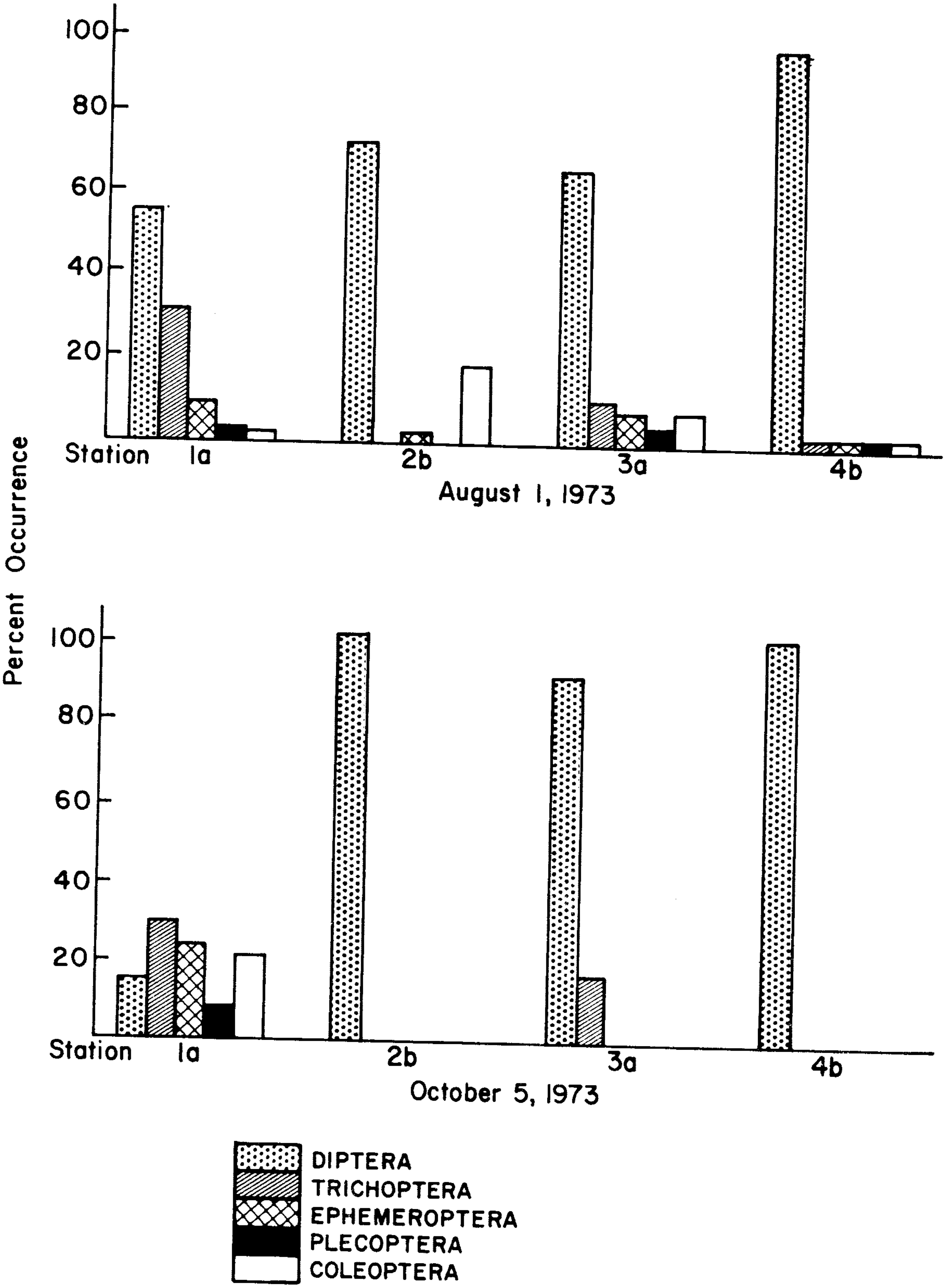

Figure 39. Percent Occurrence of Aquatic Insects by Order in Basket Samples

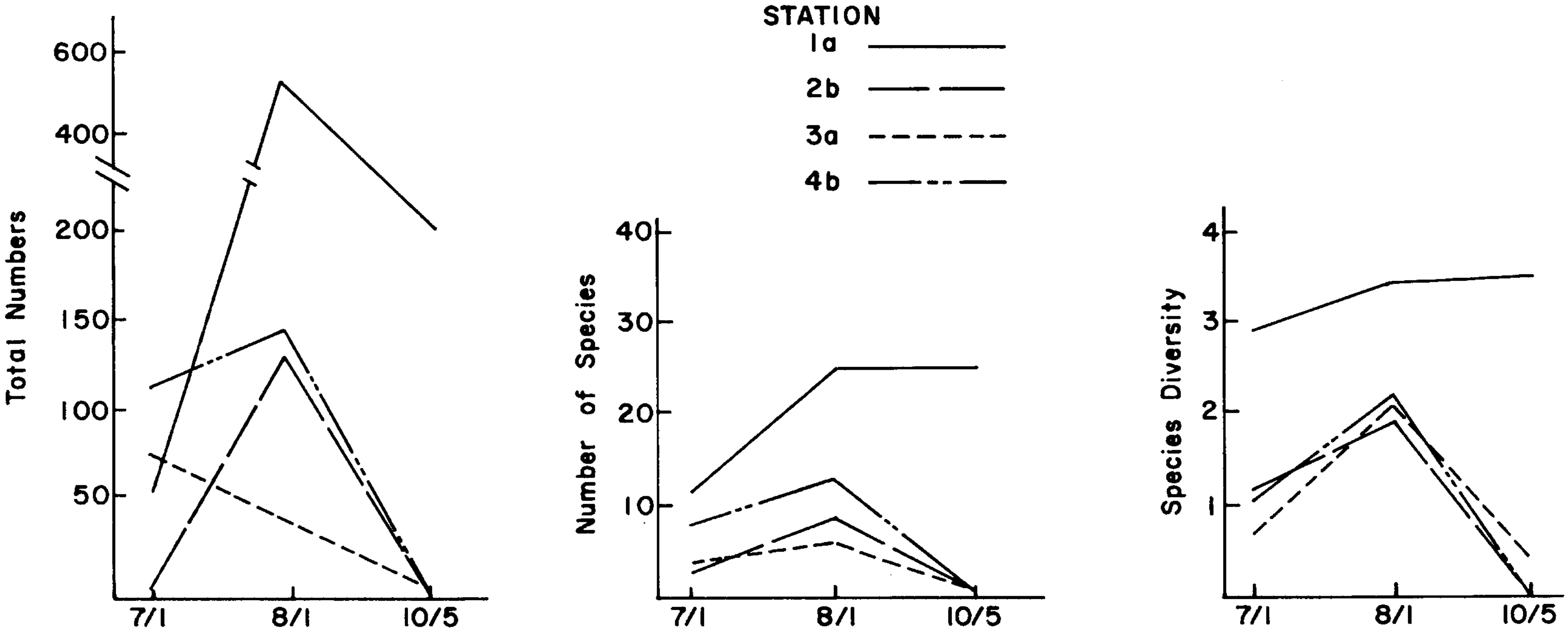

Figure 40. Changes in Macroinvertebrate Community Structure in Surber Samples During Summer, 1973 at Four Stations in the Coeur d'Alene River

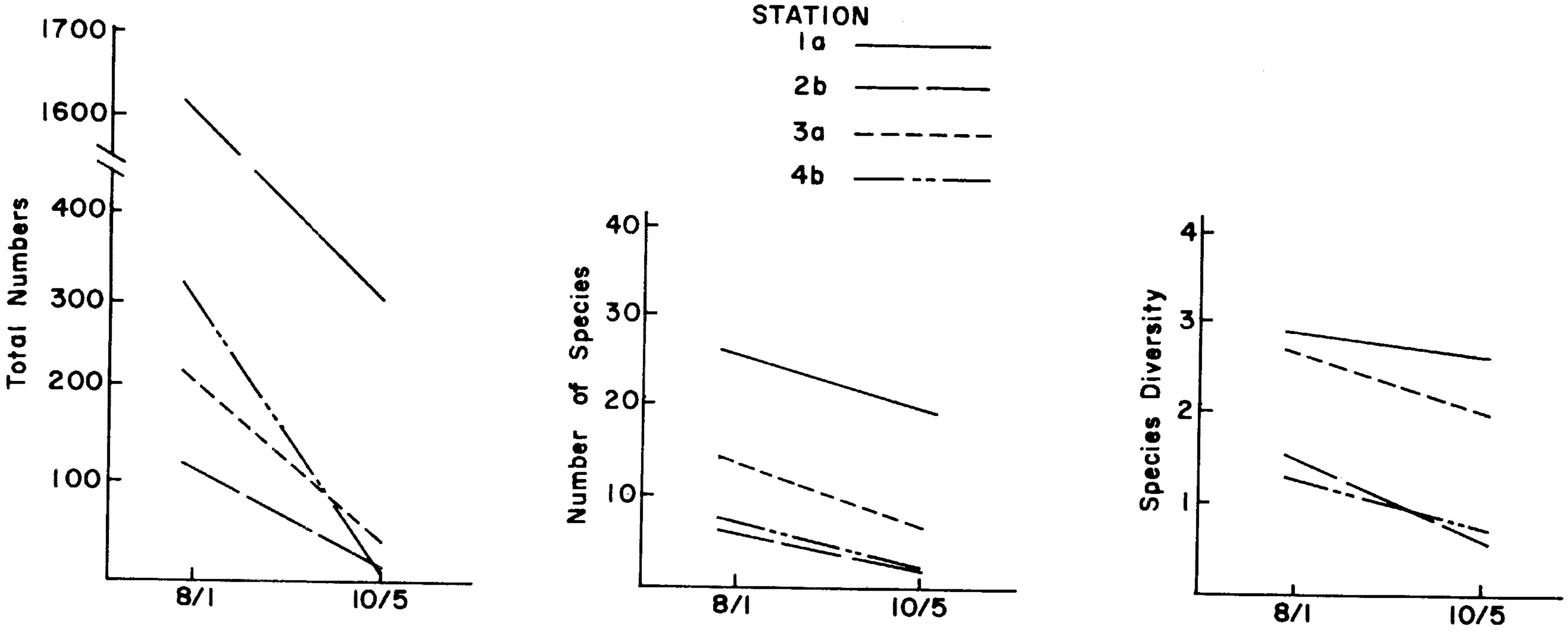

Figure 41. Changes in Macroinvertebrate Community Structure in Basket Samples at Four Stations in the Coeur d'Alene River During Summer, 1973

Table 14. Community Structure in Control (North Fork) and Test (South Fork) Baskets in the Coeur d'Alene River.

Parameter	North Fork Stones	South Fork Stones
N	595	526
s	23	22
D	2.993	2.750

E. Zinc Concentration in the Benthic Food Chain

During August 1973, aquatic insects were collected and returned to the laboratory for analysis for Zn content. The insects were maintained in the laboratory for two days to rid the gut and exoskeleton of adhering organic particles. The time limitations of our study made it impossible to carry out year-around collections of insects for testing purposes. Various species are not present during certain times of the year. For these reasons we could not make complete comparisons of differential metallic concentration by several species inhabiting this river drainage. Analytical results presented in Table 15 are for dry-weight samples of 2 to 23 mg. Replicates were run when there were enough organisms for two 10mg samples. The insects listed are categorized as primary and secondary consumers, although food sources vary considerably.

Table 15. Concentrations of Zinc in Aquatic Insects from the Coeur d'Alene River, August 1973.

Insect	North Fork (Station 1)	Main Stem (Station 4)
Primary consumers		
Ephemerella serrata	1392, 1739	
Hydropsyche sp.	202, 274	714
Chironomidae		10000, 2600
Brychius sp. (adults)		111, 174
Secondary consumers		
Acroneuria sp.	459, 426	
Atherix variegata		1367, 962
Oreodytes sp. (adults)		222

In addition to the above samples, insects previously collected and preserved in 70% isopropyl alcohol were analyzed. Organic detrital material with which the Chrironomidae especially were closely associated also was analyzed. These results and results from analysis of preserved insects from previous years, 1968-1971 (Table 16), showed considerably higher metal concentrations than the cleared insects. Organic detrital material contained the highest levels of Zn, followed by primary consumers, while secondary consumers contained the lowest levels.

Concentrations in the North Fork samples were relatively high, while samples from a second control station, Big Creek, a tributary to the South Fork, apparently contained much lower levels of Zn. The North Fork at its mouth may receive Zn from the South Fork during high flow levels or from airborne sources which persist in the food chain during the summer season. Concentrations of Zn in insects from the main stem 8 km (5 miles) below the confluence for the 1968-1971 samples were in the same order of magnitude as those from the South Fork and most likely reflect ingestion from the bottom materials rather than absorption from the water.

These results are in agreement with those of Rozhanskaya (1969), who demonstrated that benthic marine organisms contained .002- .19% of the Zn concentration present in the bottom materials but 500-3800 times the Zn content of the water. It was also found that metal concentrations declined in certain benthic feeding and predatory fish.

Table 16. Concentration of Zinc in Selected Aquatic Insects, Organic Detritus and Water from the Coeur d'Alene River and a Tributary (mg/kg dry weight).

Station	Taxon	1968	1969	1970	1971	1973	Water (mg/l)
South Fork	Chironomidae		25,200	9,330	2,547	25,000	20
Main Stem	Organic detritus					50,119	5
	Chironomidae	8,410	14,700	18,700	17,368	20,000	
	Hydropsyche sp.					13,536	
	Atherix variegata		3,130	9,820	4,316		
North Fork	Organic detritus					14,286	.01
	Chironomidae			2,080		3,000	
	Atherix variegata			595			
Big Creek	Organic detritus					424	.01
	Chironomidae					508	
	Hydropsyche sp.					820	

F. Coeur d'Alene River Study Summary

Artificial substrates in the form of rock-filled, cylindrical wire baskets were placed in clean and polluted portions of the Coeur d'Alene River during the summer of 1973. Baskets located in the clean North Fork (Station 1, Figure 24) were colonized successfully by an abundant and diverse macroinvertebrate fauna comparable to that collected by Surber sampler from the natural substrate (Tables 8-11, Figures 38-39). Baskets located at the mouth of the South Fork (Station 2) and in the main stem of the river .88 km (.4 mi) (Station 3) and 1.76 km (.8 mi) (Station 4) below the confluence showed that only a sparse fauna was present in polluted portions of the river. A moderate abundance and diversity of insects was collected in July at these stations whereas during September, coinciding with low flow levels, the size of the communities had been greatly reduced (Figures 40 and 41).

At Station 3 significantly more insects were present in the baskets than in the Surber samples indicating the substrate as a possible limiting factor at this station. Substrate analysis revealed a higher percentage of sands at this station than at all other stations, possibly resulting in compaction and reduction in hyporheal habitat (Table 6, Figure 36).

Macroinvertebrate communities at Stations 2 and 4 were similar in diversity and abundance, although more mayfly species were present at Station 4. Substrate analysis indicated that particle size distributions at these stations were similar to each other and to Station 1, with no indication of excessive fines. Both stations were located in shallow, swift-flowing riffles comparable to the North Fork site.

Colonized baskets from the North Fork were placed in the South Fork on September 15. Within two weeks, the community was reduced from 227 individuals and 18 species to 49 individuals and 4 species--two midges, a trichopteran (Hydropsyche sp.) and a tipulid (Antocha sp.) (Table 13). Based on these tests, it seems apparent that water quality rather than substrate conditions was the critical inhibiting factor on recovery of the benthic macroinvertebrate community in the South Fork and main stem.

The water chemistry of this area is itself a complex of many dissolved elements which alone or in combination may be toxic to the benthic fauna. While heavy metal concentrations were high (up to 23 mg/l Zn and .35 mg/l Cd), it has been demonstrated that many aquatic insects are tolerant of these conditions. Fluoride concentrations of 6.8 mg/l in the South Fork and 2.4 mg/l below the confluence may be the most critical water quality parameters affecting insect survival. Oxygen and temperature levels were well within acceptable levels for aquatic life. Nutrient levels were high, contributing to a dense algal biomass.

Periphytic algae growth at Station 2 in the South Fork exceeded that at all other stations (Table 4, Figure 34) and consisted almost entirely of Chlorella sp. The periphyton communities present below the confluence consisted of approximately 30% diatoms and 70% Chlorella, while the North Fork community was made up almost entirely of diatoms. Large amounts of particulate organic matter were observed in conjunction with the algal samples at the polluted water stations. The periphytic algae in the South Fork and main stem were predominantly an epipelic form colonizing the deposits of fine inorganic and organic detritus present on the substrate. This material was disturbed easily by current movement, turbulence and any other interference and may have accounted for the continued greenish, turbid appearance of the water in the main stem of the river.

Analysis of organic detritus and insect tissue for concentrations of metals was conducted. Concentrations were highest in organic detritus (up to 50,000 mg/1 dry weight), followed by primary consumers such as Chironomidae larvae, and were lowest in secondary consumers such as the predaceous fly larvae of *Atherix variegata* (Table 16). Metal levels in insects collected from the North Fork were quite high, while insects collected from a second control station in Big Creek, a tributary to the South Fork, were low. No evidence of magnification through the food chain was demonstrated.

II. Lateral Lakes Along Coeur d'Alene River

A. Water Quality

Physicochemical Conditions

During the spring months, the water level along the main stem of the Coeur d'Alene River is usually above the surface of the adjacent valley floor, and the non-diked areas along the river form one continuous body of water. Precipitation during the winter of 1973 was relatively light, resulting in lower streamflow that reached bank level but rose no higher. At the time of initial sample collection, water from the river still was flowing into the lakes. Shortly thereafter, the water level stabilized throughout the main stem and lateral lakes region until fall. In September, the water level in the main stem was drawn down by releases from the Post Falls Dam on the Spokane River which, in turn, resulted in the rapid drop of water levels in the lateral lakes region.

Seven of the nine lakes are connected to the river by a channel. The other two, Cave and Rose Lakes,have no direct connection (Figure 42).

Stations for water and sediment samples were located at increasing distances away from the inlets (Figures 1 and 42). Station 1 is at the mouth of each lake inlet; Stations 2-4 are open-water stations. The depth of these stations ranged from 1 to 9 m.

The lakes on the south side of the river including Cave Lake, are separated from the main stem by a railroad levee. On the northwest side of Cave Lake, however, there are open spaces in this levee which serve as a connection to the river during high water. Cave Lake also is connected to Medicine Lake by a small channel. The inlets into the lakes on this side of the river are all long and winding.

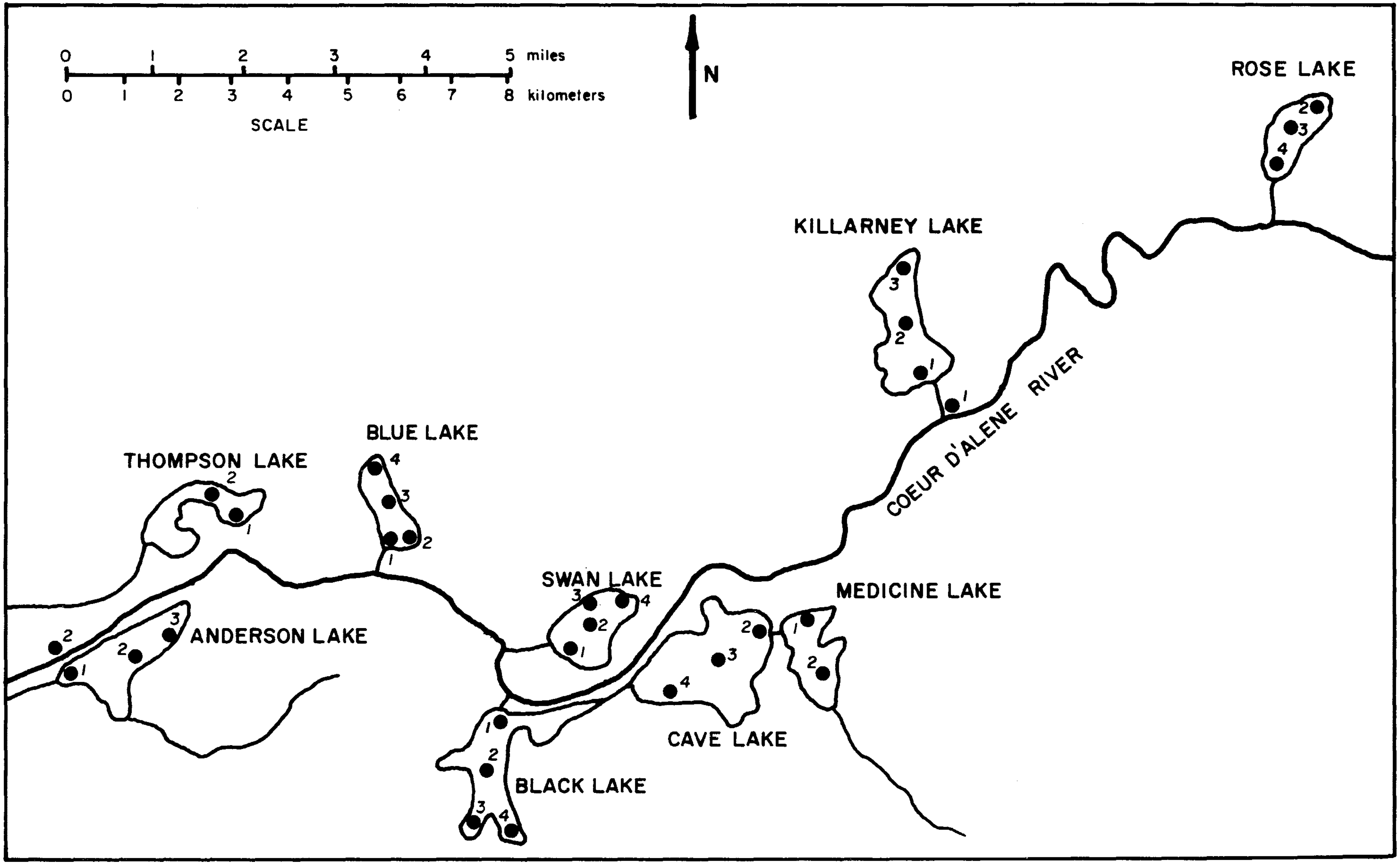

Figure 42. Station Locations in the Coeur d'Alene River Valley Lakes

Of the lakes on the north side of the river, Blue, Swan and Killarney Lakes have no barriers between the river and their borders. Rose Lake is separated from the river by the state highway; however, river water can move through the culverts and seep across the marsh into the lake. Thompson Lake is separated from the river by a gravel road and has a straight dredged-out channel and a much wider inlet than the other lakes.

The Coeur d'Alene River stations were located near Killarney and Anderson Lakes (Figure 42). Bells Lake, a control station, was located on the St. Joe River, 27 km (17 miles) upstream from the St. Joe River delta in Lake Coeur d'Alene.

The water in the lateral lakes was clear at the time of sampling (May-June 1973) except near the inlets, where it was turbid. In Thompson and Anderson Lakes, the green-colored river water could be traced easily into the lakes for about 100 m.

The lakes were very uniform in chemical composition, containing low levels of dissolved substances (Table 17). Specific conductance ranged from 55-92 micromhos, hardness from 14-22 mg/1 $CaCO_3$ and methyl orange alkalinity from 11-23 mg/1 $CaCO_3$. The pH was always at or near 7.0. Dissolved oxygen at the surface was near saturation, and dissolved oxygen near the bottom was not below 4 mg/1.

In the spring, Cd, Cu and Pb in the water were below Atomic Absorption Analysis (AAS) detection limits, while Zn measurements varied within lakes.

At the inlets (Station 1) in Thompson, Swan and Anderson Lakes, Zn concentrations were similar to the Zn level in the river (.41 mg/1, Table 17). Analysis of water samples at that time, from open-area

Table 17. Chemical Characteristics of the Coeur d'Alene River Valley Lakes and the Coeur d'Alene River Main Stem, Spring 1973. (Station 1 in each case was located at the inlet, Stations 2-4 were open-water stations.)

Station		Date	T (C)	pH	D.O. (mg/l)	Conductivity (micromhos)	M.O. Alk. (mg/l $CaCO_3$)	Hardness (mg/l $CaCO_3$)	Ca	Mg	Zn
Rose Lake	2	6/21/73	22	7.0	--	80	14	15.6	3.3	1.8	0.05
	3	6/21/73	22	7.0	--	80	11	15.4	3.2	1.8	0.05
	4	6/21/73	22	7.0	--	80	14	15.6	3.3	1.8	0.05
Killarney Lake	1	6/12/73	20	7.0	7.0	80	16	20.6	4.6	2.2	0.24
	2	6/12/73	20	7.0	7.0	78	15	20.6	4.6	2.2	0.22
	3	6/12/73	20	7.0	6.5	78	17	20.6	4.6	2.2	0.22
Medicine Lake	1	6/13/73	21	7.0	8.0	55	15	12.8	2.8	1.4	0.05
	2	4/14/73	11	7.0	10.0	60	11	10.2	2.1	1.3	0.06
	3	4/14/73	12	7.0	--	60	12	9.6	1.9	1.2	0.06
Cave Lake	2	6/11/73	22	7.0	8.0	60	18	16.7	3.9	1.7	<0.05
	3	6/11/73	22	7.0	7.0	60	15	16.7	3.9	1.7	<0.05
	4	6/11/73	22	7.0	8.0	60	15	16.7	3.9	1.7	<0.05
Swan Lake	1	5/28/73	14	7.0	--	80	17	18.5	3.6	2.2	0.44
	2	5/28/73	19	7.0	--	75	14	17.7	3.6	2.1	0.07
	3	5/28/73	19	7.0	--	75	14	17.7	3.6	2.1	0.07
	4	5/28/73	19	7.0	--	78	14	17.7	3.6	2.1	0.07
Black Lake	1	5/31/73	19	7.0	7.8	90	20	21.7	4.2	2.7	0.09
	2	5/31/73	19	7.0	7.8	90	22	21.6	4.2	2.7	0.04
	3	5/31/73	19	7.0	7.8	92	23	21.8	4.2	2.8	0.04
	4	5/31/73	19	7.0	7.8	90	21	22.2	4.2	2.9	0.04
Blue Lake	1	5/30/73	21	7.0	7.8	73	13	15.7	3.3	1.8	0.12
	2	5/30/73	21	7.0	7.3	70	14	14.2	2.9	1.7	0.06
	3	5/30/73	21	7.0	7.8	70	14	14.2	2.9	1.7	0.07
	4	5/30/73	21	7.0	7.8	72	14	14.3	2.9	1.7	0.06
Thompson Lake	1	5/17/73	14	7.0	6.0	60	15.5	14.5	2.9	1.7	0.41
	2	5/17/73	20	7.0	8.0	90	15	15.6	2.9	2.1	0.06
Anderson Lake	1	5/18/73	14	6.8	5.0	60	14.4	14.2	2.9	1.6	0.34
	2										
	3	5/18/73	20	7.0	8.0	80	14.4	17.6	3.7	2.4	0.05
Coeur d'Alene River	1	6/13/73	16	7.0	6.5	100	20	25.9	5.6	2.9	1.10
	2	5/17/73	14	7.0	6.5	60	14	14.4	2.9	1.6	0.41

stations of the same lakes, gave values near .06 mg/l. Zinc levels in Black and Blue Lakes were also uniform throughout the lakes while increasing to .09 and .12 mg/l respectively near the inlets.

The level of Zn in the open waters of Killarney Lake was the same as at the inlet, .22 mg/l. The wide inlet apparently transports a larger volume of river water into this lake, and the drop in Zn concentration that was observed in other lakes did not occur. The concentration of Zn in the river near Killarney was 1.1 mg/l. A higher level of Zn was not measured at the inlet station, possibly because of previous mixing action of river and lake water in the inlet area.

In Rose and Cave Lakes, Zn concentrations were below detection limits at all the stations. Neither of these lakes has a direct connection to the river.

In October, when the water level was low in the river, the Zn concentration rose to 6.3 mg/l at Station 2. At the inlet (Station 1) of Anderson Lake and the open-water stations of Anderson (Station 3) and Thompson (Station 2) Lakes, the Zn concentration was less than .05 mg/l. In Thompson Lake, the Zn level was .15 mg/l at the inlet (Station 1).

In January, the level of Zn in the river dropped to 1.6 mg/l with a rise in the water level caused by winter rains. The Zn concentration in Thompson Lake was unchanged from the October samples at the two stations. However, in the open-water samples of Anderson Lake (Station 3), the Zn concentration rose to .25 mg/l.

The preceding information indicates how closely the water quality in the lakes is dependent on the river and how easily conditions in the lakes can change due to fluctuating water levels.

B. Lateral Lake Sediment Analysis

Lee (1970) stated that, in most lakes, mixing of sediments occurs in the upper 5 cm, and at least partial mixing may occur in the 5 to 15 cm zone. The top 2 to 3 cm sample taken from the lateral lakes probably represents a composite of the sedimentation that occurred over a number of years.

Heavy metal analysis of the sediments from the lateral lakes is listed in Table 18 for Atomic Absorption Analysis (AAS) and Table 19 for Neutron Activation Analysis. The levels of Zn, Cu, Cd and Pb in the sediments indicate a definite deposition of heavy metals over background levels such as occur in Bells Lake. The sediments there contained 50-110 mg Zn/kg and 30 mg Pb/kg. Levels of Zn and Pb in the Coeur d'Alene lakes were 10-40 times higher than in Bells Lake. Copper and Cd levels were not increased to the same extent, but show a definite increase over Bells Lake's sediments. Bowen (1966) lists the worldwide averages of Cu, Pb, Zn and Cd in the soil as 20, 10, 50 and .06 mg/kg, respectively. Canney (1959) cites estimates of background levels in the Coeur d'Alene area soil for Cu, Pb and Zn, as 25, 20 and 100 mg/kg, respectively.

The distribution of metals in the lake sediments reflects the mode of deposition from the river. There was a general decreasing trend in the concentration of Zn, Cu, Pb and Fe away from inlet stations (Table 18).

In the inlet-connected lakes, however, the highest levels often occurred at Station 2. This likely is due to the higher adsorption of metals onto the sediments at these stations. Thomas (1972) found that Hg adsorbed to fine silty clays and organic sediments in greater amounts than on coarse inshore sediments. In the Coeur d'Alene lakes, the inlet

Table 18. Metals in the Sediments of the Coeur d'Alene River Valley Lakes Determined by Atomic Absorbtion Analysis. (Station 1 in each case was located at the inlet, stations 2-4 were open water stations.)

Station	Depth (m)	Zinc (mg/l)	Copper (mg/l)	Cadmium (mg/l)	Lead (mg/l)	Iron (%)
Rose	2 (1)[1]	240	21	2	100	0.5
Lake	3 (5)	1900	23	14	2150	3.3
	4 (5)	2100	38	15	3200	3.9
Killarney	1 (4)	4000	140	50	4600	9.3
Lake	2 (5)	4250	160	55	3950	9.0
	3 (2)	5200	87	130	2550	4.6
Medicine	1 (1)	2550	79	30	3000	8.7
Lake	2 (6)	2950	87	44	2650	6.5
Cave	2 (3)	2750	29	45	2300	2.2
Lake	3 (6)	2800	60	34	2700	4.0
	4 (8)	3300	79	29	3850	5.5
Swan	1 (1)	2600	112	25	3500	10.0
Lake	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	1 (1)	2350	92	29	4700	8.5
Lake	2 (9)	2600	38	29	1750	4.2
	3 (5)	2300	13	18	800	2.1
	4 (2)	1750	8	11	490	1.6
Blue	1 (1)	2000	126	25	3400	9.2
Lake	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	1 (2)	3250	76	46	2850	7.0
Lake	2 (5)	3550	87	42	3350	4.1
	3 (3)	2150	34	56	1750	2.5
Bell's	2 (4)	110	4	2	30	2.2
Lake	3 (6)	52	8	2	300	2.4
	4 (3)	100	9	2	300	2.0

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[1] The number in parenthesis is the depth in meters.

Table 19. Metals in the Sediments of the Coeur d'Alene River Valley Lakes Determined by Neutron Activitation at WSU Nuclear Radiation Center. (Station 1 was located at the inlet, Stations 2-4 were open-water stations.)

Station	Depth (m)	Ce mg/kg	Lu µg/kg	Se µg/kg	Th µg/kg	Cr mg/kg	Hf mg/kg	Ba mg/kg	Zr mg/kg	Sb µg/kg	Cs mg/kg	Tb µg/kg	Sc µg/kg	Rb mg/kg	Fe (%)	Zn mg/kg	Ta µg/kg	Co mg/kg	Eu mg/kg
Killarney	1 (4)[1]	83	698	1063	8,596	26.5	5.0	667	261	67,224	6,370	1,476	6,855	109	6.9	3849	608	11.1	2.5
Lake	2 (5)	99	817	1705	10,357	45.0	3.6	817	222	118,564	10,718	402	9,518	166	7.6	4430	775	23.9	2.7
	3 (2)	101	696	1312	10,473	43.6	3.7	825	139	81,386	8,964	1,459	10,918	136	4.6	4984	738	16.1	2.2
Medicine	1 (1)	86	757	918	8,214	25.0	5.1	640	260	59,998	5,565	2,029	6,950	111	7.2	2710	628	13.3	2.3
Lake	2 (6)	104	638	1395	11,642	49.0	3.6	922	217	78,398	10,928	1,579	12,720	181	5.7	2605	852	18.1	2.6
Cave	2 (3)	125	774	1679	11,756	35.7	6.2	725	344	28,220	7,238	677	9,839	113	2.95	2373	867	11.0	2.4
Lake	3 (6)	103	610	1211	11,170	41.3	4.0	740	223	44,931	9,244	458	10,586	128	4.6	2712	793	12.1	2.3
Swan	1 (1)	72	695	1221	8,140	24.7	5.9	638	345	79,125	5,138	1,049	5,754	115	10.2	3152	574	15.6	2.8
Lake	2 (6)	77	675	1188	9,348	36.0	3.9	812	223	91,338	8,666	1,728	8,695	136	8.4	3068	656	18.9	2.7
	3 (3)	98	711	1272	10,199	44.0	3.4	1025	187	121,043	10,823	1,225	9,887	180	7.6	5503	726	25.5	2.6
	4 (2)	82	593	1016	8,036	22.7	6.1	524	278	35,660	4,653	964	6,318	82	6.1	2006	763	9.1	2.2
Black	1 (1)	87	636	1012	8,283	24.0	6.2	769	311	64,994	4,950	1,337	5,989	116	8.7	2673	625	16.2	3.0
Lake	2 (9)	104	780	1304	11,514	50.0				48,823	10,116	522	16,450	187	5.9	3157	996	18.3	2.5
	3 (5)	57	793	730	6,728	21.1	5.7	578	305	62,150	4,789	3,358	6,852	119	10.2	3398	658	11.6	2.4
	4 (2)	94	744	1379	9,805	42.0	4.5	852	238	16,458	5,993	600	13,176	109	3.0	1760	1078	11.3	2.4
Blue	1 (1)	92	664	1490	8,213	32.9	4.1	640	213	107,056	6,456	1,473	6,891	115	9.0	2094	641	14.7	2.8
Lake	2 (2)	92	821	1436	9,593	38.3	3.6	779	211	104,334	9,513	1,271	9,055	141	5.3	8505	736	16.4	2.5
	3 (8)	140	707	1393	12,001	43.5	4.3	770	240	24,750	9,460	1,629	13,097	136	3.3	3093	902	15.0	2.4
	4 (3)	95	800	1257	10,370	41.8	3.3	892	238	93.656	12,149	898	10,866	177	5.9	3973	730	20.7	2.4
Thompson	1 (1)	67	698	639	6,528	20.6	3.9	640	191	57,978	9,521	403	10,933	147	5.9	2796	880	11.8	2.5
Lake	2 (3)	96	655	1352	11,215	42.0	3.8	898	261	66,301	4,712	285	4,645	101	8.1	3611	562	13.7	2.5
Anderson	1 (2)	86	920	1337	8,913	27.3	6.5	756	331	73,512	5,903	439	6,327	118	8.6	3215	681	16.0	2.8
Lake	3 (3)	88	690	1310	9,510	29.4	6.4	644	303	27,265	4,955	986	9,345	81	2.5	2531	863	9.0	2.2
Coeur d'Alene	1 (5)	72	703	559	6,195	17.6	3.7	601	178	56,380	4,300	3,553	6,669	112	8.6	5651	596	9.0	2.5
River	2 (1)	58	838	1094	6,818	22.0	5.6	619	297	62,054	4,637	1,348	5,328	119	10.0	3321	639	10.8	2.4

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[1] The number in parentheses is the depth in meters.

stations contained 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 away from the inlets.

Rose and Cave Lakes, as previously mentioned, are not directly connected to the river, but they show the same decreasing pattern. In Rose Lake, the concentration of the metals is lowest at Station 2, which is the sampling point furthest removed from the river. (This phenomenon also suggests seepage.) In Cave Lake, the metals increase from Station 2 to Station 4 and emphasize the importance of the opening in the levee on the northwest side of the lake as a source of river water.

The metal content of the sediments in Medicine and Killarney Lakes does not follow this pattern. In Medicine Lake, the distance between Station 1 and Station 2 is probably not great enough to get a drop in metal concentration. In Killarney Lake, the distribution of Zn and Cd in the sediments is opposite to the general trend. This variant pattern most likely is dependent on the greater transport of river water into the lake caused by the wider inlet.

Zinc and Fe levels were used in comparing AAS and neutron activation analysis of the sediments. Zinc levels reported by neutron activation were generally higher than levels measured by AAS, some differing by as much as 30% but most by much less (Tables 18 and 19). We recorded the same trend in Coeur d'Alene Lake sediment cores in our previous studies (Funk, Rabe, Filby _et al._, 1973). In a number of the lateral lakes, similar results in Fe content were noted.

Of the other elements listed in Table 19, only Cs and Sb are higher than the average levels in soils listed by Bowen (1966). Bowen gives the average soil content of Cs as 6 (.3-25) mg/kg and Sb as 2-10 mg/kg dry weight. He states that Cs is relatively harmless, while Sb is moderately toxic. These metals in the lateral lakes sediments ranged from 4-1,000 mg/kg for Cs and 16-121 mg/kg for Sb.

C. Lateral Lake Fish Analyses

Some fish samples analyzed were below AAS detection limits for Cu and Cd. These limits depend in part on the amount of tissue available for analysis and on the volume of 5% HNO_3 used for dilution of the ash. Only the fish samples analyzed which were above these detection limits are included in the results. The means listed for Cu and Cd therefore were biased upward by a slight amount.

Yellow perch (Perca flavescens) were used to compare levels of metals in fishes from different locations. The mean levels of Zn, Cu and Cd in yellow perch from five Coeur d'Alene River lakes, the Coeur d'Alene River and Bells Lake are listed in Tables 20-22. The levels of these metals in five different fish species from the Coeur d'Alene River lakes are listed in Tables 20-25. The Analysis of Variance Summary Tables given in Appendix B, Tables B-1 and B-2, for this data indicate that there were significant differences. Duncan's Multiple Range Test was used to determine what these differences were. Liver-to-muscle ratios (L/M) were calculated as an additional means of comparing metals in fishes by indicating the relative distribution of the metal in the fish.

Comparison by Lakes of Metals in Fish Tissue

Zinc:

Levels of Zn in muscle tissue of yellow perch varied slightly from lake to lake (Table 20). Zinc levels in fish from Rose, Killarney and

Black Lakes were similar to levels found in Bells Lake's fish (47 mg/kg); levels in fish from Blue Lake were slightly higher (NS)[1] and those in fish from Coeur d'Alene River and Swan Lake were significantly higher than in fish from the other lakes (Coeur d'Alene not sig. from Blue).

The mean Zn level in the liver tissue for yellow perch from Rose Lake (S) and Bells Lake (NS) were less than levels found in fish from other stations along the river (54 and 77 mg/kg as compared to 132-176 mg/kg).

Copper:

Levels of Cu in perch from all the locations were similar, ranging from .26- .62 mg/kg in muscle and 2.8-6.1 mg/kg in liver tissue (Table 21). However, fish from Killarney Lake had higher levels (S) in both muscle and liver, with a L/M ratio of 42.

Cadmium:

Cadmium levels in muscle tissue were similar in perch from the lateral lakes and Bells Lake .18- .50 mg/kg) (Table 22). Samples from Coeur d'Alene River were (S) higher (X = .77 mg/kg). Cadmium levels in the liver, however, varied substantially. Liver samples of fish from Rose Lake and Bells Lake were less (NS) than in the other lakes. Cadmium in the liver of fish from Killarney Lake was significantly higher, with a L/M ratio of 240.

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[1] The abbreviations: S = Significant; NS = Not Significant.

Table 20. Concentration of Zinc in Yellow Perch (mg/kg) from Lateral Lakes, Coeur d'Alene River and Control Station (Bell's Lake, St. Joe River Drainage).

Stations Lateral Lakes	Mean Wt.	Tissue	Mean Zn (mg/kg	95% C.I.	Range	N[1]	Liver/Muscle Ratio[2]
Rose Lake	33.6 g	muscle	44.6	±5.4	29.9- 52.9	12	1.2
		liver	54.0	±9.6	30.0- 73.1	13	
Killarney Lake	97.3 g	muscle	47.3	±10.7	38.5- 54.1	4	3.5
		liver	165.5	±33.7	134.3-181.7	4	
Black Lake	44.9 g	muscle	49.5	±5.1	34.1- 63.0	13	2.7
		liver	132.4	±38.3	55.9-257.1	13	
Swan Lake	32.7 g	muscle	102.1	±19.4	70.2-119.1	6	1.4
	68.3 g	liver	140.2	±78.8	62.5-283.0	6	
Blue Lake	33.6 g	muscle	65.8	±11.2	53.3- 91.6	8	2.3
		liver	149.2	±43.6	58.3-227.8	8	
Coeur d'Alene River	39.7 g	muscle	72.6	±19.0	40.3-121.8	10	2.4
		liver	176.9	±75.6	94.0-447.0	10	
Bell's Lake (Control)	29.0 g	muscle	46.7	±20.0	37.5- 52.5	3	1.7
		liver	77.3	±65.2	48.1- 98.9	3	
Overall Mean		muscle	58.3	±6.8		43	2.0
		liver	116.4	±13.8		44	

[1] Number of fish analyzed above AAS detection limits.

[2] Liver to muscle ratios on given means.

Table 21. Concentration of Copper in Yellow Perch in mg/kg Dry Weight.

Stations Lateral Lakes	Mean Wt.	Tissue	Mean Cu (mg/kg)	95% C.I.	Range	N[1]	Liver/Muscle Ratio[2]
Rose Lake	33.6 g	muscle	0.44	±0.05	0.35- 0.63	12	6.4
		liver	2.8	±1.3	1.70- 5.9	7	
Killarney Lake	97.3 g	muscle	1.06	±0.54	0.68- 1.4	4	42.0
		liver	44.5	±26.9	24.00-64.9	4	
Black Lake	44.9 g	muscle	0.36	±0.10	0.20- 0.64	9	13.9
		liver	5.0	±3.8	1.90- 7.1	4	
Swan Lake	32.7 g	muscle	0.62	±0.38	0.44- 1.17	5	8.7
	68.3 g	liver	5.4	±3.2	4.60- 6.9	3	
Blue Lake	33.6 g	muscle	0.46	±0.10	0.26- 0.70	8	12.8
		liver	5.9	±2.5	2.80-10.9	7	
Coeur d'Alene River	39.7 g	muscle	0.48	±0.06	0.39- 0.54	6	12.7
		liver	6.1	±2.3	3.60- 8.6	5	
Bell's Lake (Control)	29.0 g	muscle	0.26	±0.03	0.25- 0.26	3	22.3
		liver	5.8	±8.5	3.10- 9.6	3	
Overall Mean		muscle	0.52	±0.07		38	21.3
		liver	11.00	±6.7		25	

[1] Number of fish analyzed above AAS detection limits.

[2] Liver to muscle ratios on given means.

Table 22. Concentration of Cadmium in Yellow Perch in mg/kg Dry Weight.

Stations Lateral Lakes	Mean Wt.	Tissue	Mean CD (mg/kg)	95% C.I.	Range	N[1]	Liver/Muscle Ratio[2]
Rose Lake	33.6 g	muscle	0.21	±0.03	0.17- 0.28	8	11.9
		liver	2.50	±0.42	1.60- 3.80	12	
Killarney Lake	97.3 g	muscle	0.37	±0.14	0.31- 0.50	4	240.5
		liver	89.00	±7.50	85.50-91.00	3	
Black Lake	44.9 g	muscle	0.29	±0.06	0.17- 0.42	9	30.7
		liver	8.90	±3.50	2.30-21.20	12	
Swan Lake	32.7 g	muscle	0.50	±0.24	0.22- 0.85	6	42.8
	68.3 g	liver	21.40	±12.90	5.20-36.50	6	
Blue Lake	33.6 g	muscle	0.26	±0.05	0.21- 0.32	6	54.2
		liver	14.10	±4.50	6.40-22.50	7	
Coeur d'Alene River	39.7 g	muscle	0.77	±0.43	0.18- 2.00	10	28.0
		liver	21.60	±7.80	10.10-34.00	9	
Bell's Lake (Control)	29.0 g	muscle	0.18			1	8.3
		liver	1.50	±1.10	0.38- 2.60	2	
Overall Mean		muscle	0.31	±0.01		33	50.4
		liver	15.80	±7.30		40	

[1] Number of fish analyzed above AAS detection limits.

[2] Liver to muscle ratios on given means.

The difference observed in metal content in fish from the lateral lakes appears to be somewhat correlated to the lakes' connections with the river. The similarity found likely is dependent on the fish's ability to regulate the metal content in its tissues and most likely would tend to decrease the expected differences between locations.

The levels of metals in perch from Rose Lake--which is not directly connected to the river--are most similar to concentrations found in fish from Bells Lake (control station on St. Joe River drainage). Liver and muscle tissue of fish from all lakes tested contained Zn and Cu in excess of those levels found in Bells Lake's fish. Perch from Killarney Lake contained levels of Cu and Cd that were distinctly higher than fish from other lateral lakes. The increased metals in fish tissue of Killarney Lake probably reflect the lake's proximity to the source of contamination, the South Fork of the Coeur d'Alene River, together with the larger volume of river water entering the lake by way of a wider inlet.

Comparison of Fish Species

Zinc:

The mean Zn levels in the muscle tissue of five species of fishes from the Coeur d'Alene River lakes ranged from 12.5-67.6 mg/kg (Table 23). Bullheads (Ictalurus nebulosus) contained higher concentrations in the muscle (NS) and liver (S). Largemouth bass (Micropterus salmoides) had significantly lower levels in the muscle tissues.

Copper:

The level of Cu in muscle tissue, with an overall mean of 1.2 mg/kg, was similar in four species (Table 24); but in yellow perch it was significantly less. Copper levels in the liver of the black crappie (Pomoxis nigromaculatus) (41.3) and bullheads (39) were higher (S) than levels in the other species.

Cadmium:

Cadmium levels, which averaged .47 mg/kg in the muscle of the five species, were not significantly different (Table 25). Levels in the liver tissue ranged from 3.8 in bullheads to 24.5 in crappie, which was (S) higher than in other species except bass.

Levels of Zn in muscle differed in the species of fishes sampled, while Cu and Cd levels in muscle were fairly similar in the five species. The observed differences for Zn may be attributed either to differences in trophic level of the fish species or to differences in the body weight of the fish analyzed, which may affect the Zn accumulation.

The fish species from the lateral lakes can be ranked roughly according to their trophic level from omnivorous to carnivorous in the following order: bullheads → yellow perch → pumpkinseed → black crappie→ largemouth bass. Zinc in muscle decreases along this rank from 67.6 mg/kg in bullheads to 12.5 mg/kg in largemouth bass (Table 23). This trend may be due to the Zn content of the food consumed by the different species. It has been observed generally, for metals other than Hg, that there is a decrease in levels of metals up the food chain in aquatic environments (Rozhanskaya, 1969; Baptist and Lewis, 1969; Windom et al., 1973; Mathis and Cummings, 1971; Funk et al., 1973). Therefore, fishes that feed at a higher trophic level consume material that contains lower levels of metals.

Table 23. Concentration of Zinc (mg/kg dry weight) in Five Species of Fishes From the Coeur d'Alene Valley Lakes.

Species	Mean Wt.	Tissue	Mean	95% C.I.	Range	N[1]	Liver/Muscle Ratio[2]
Pumpkinseed	46.8 g	muscle	51.4	±14.6	18.5-126.4	16	2.7
		liver	107.2	±29.5	36.9-219.4	15	
Yellow Perch	43.8 g	muscle	51.0	±4.0	29.9- 91.6	38	2.3
		liver	16.4	±18.7	30.0-283.0	45	
Black Crappie	127.5 g	muscle	39.7	±4.0	32.6- 50.1	10	3.8
		liver	147.9	±8.6	86.4-230.0	10	
Bullhead	106.8 g	muscle	67.6	±6.5	18.1-262.3	19	7.4
		liver	232.1	±17.9	121.9-426.2	12	
Largemouth Bass	500.8 g	muscle	12.5	±16.5	11.9- 27.8	4	8.4
		liver	28.4	±8.5	122.8-134.8	4	
Overall Mean		muscle	51.6			87	
		liver	135.2			86	

[1] Number of fish analyzed above AAS detection limits.

[2] Liver/muscle ratio is the average from individual fish.

Table 24. Concentration of Copper (mg/kg dry weight) in Five Species of Fishes From the Coeur d'Alene River Valley Lakes.

Species	Mean Wt.	Tissue	Mean	95% C.I.	Range	N[1]	Liver/Muscle Ratio[2]
Pumpkinseed	46.8 g	muscle	1.6	±2.8	0.31- 9.8	8	5.5
		liver	8.8	±2.6	3.80- 14.5	10	
Yellow Perch	43.8 g	muscle	0.45	±0.06	0.20- 1.4	34	10.1
		liver	4.6	±1.1	1.70- 64.9	21	
Black Crappie	127.5 g	muscle	2.2	±1.3	0.28- 5.1	10	56.3
		liver	41.3	±4.5	5.00- 81.1	10	
Bullhead	106.8 g	muscle	1.6	±0.13	0.26- 3.6	16	15.5
		liver	39.0	±4.5	12.80-100.5	12	
Largemouth Bass	500.8 g	muscle	2.4	±2.2	0.42- 3.5	4	15.2
		liver	21.9	±9.6	15.70- 29.0	4	
Overall Mean		muscle	1.2			72	
		liver	20.3			57	

[1] Number of fish analyzed above AAS detection limits.

[2] Liver/muscle ratio is the average from individual fish.

As an example, bullheads are at a distinctly lower trophic level than largemouth bass. The bullheads feed on benthic insects, plankton and aquatic plants, while the bass feed almost exclusively on fish (Marcuson, 1966). The level of Zn in the bullheads was consequently much higher than Zn in the bass. The yellow perch and crappie are intermediate between these two extremes, being basically carnivorous on plankton and benthos.

The lower levels of Zn in bass from the Coeur d'Alene drainage also may be attributed to the size of the fish. The individual bass analyzed are much larger than the other species sampled (Table 23). Other investigators have found a decrease in metal content in the muscle as the size of fish increased. O'Rear (1971) found a decrease in Zn and Cu with size in striped bass (*Morone saxitilis*) weighing less than 15 grams. Cross *et al.*, (1973) found a negative correlation with body weight in a morid (*Antimora rostrata*), but no correlation to body weight in bluefish, *Pomatomus saltatrix*.

D. Lateral Lake Benthic Insect Analysis

Various aquatic insects sampled from the bottom substrate of Anderson Lake were analyzed for metal content (Table 26). Only chironomids were obtained in quantities large enough for analysis at three stations in the lake. Cadmium was below detection limits. The levels of Zn and Cu in the insects were higher than concentrations in fish flesh. As shown by Table 26, the Zn and Cu levels in the chironomids decreased in insects collected at distances further from the inlet but not in direct correlation with the levels of Zn and Cu in the sediments.

Cordulia sp. (Libellulidae), a predaceous dragonfly nymph, contained lower levels of Zn and Cu than the other insects, which follows the

Table 25. Concentration of Cadmium (mg/kg dry weight) in Five Species of Fishes From the Coeur d'Alene River Valley Lakes.

Species	Mean Wt.	Tissue	Mean	95% C.I.	Range	N[1]	Liver/Muscle Ratio[2]
Pumpkinseed	46.8 g	muscle	0.66	±1.0	0.51- 3.8	8	16.4
		liver	11.6	±5.4	2.30-33.5	11	
Yellow Perch	43.8 g	muscle	0.32	±0.05	0.17- 0.85	34	30.4
		liver	9.7	±2.9	1.60-36.3	38	
Black Crappie	127.5 g	muscle	1.1	±1.8	0.33- 3.7	5	30.4
		liver	24.5	±4.0	4.90-55.1	10	
Bullhead	106.8 g	muscle	0.17	±0.03	0.165-0.17	2	22.7
		liver	3.8	±2.8	1.30- 6.4	6	
Largemouth Bass	500.8 g	muscle	1.01	±0.89	0.11- 1.9	2	12.4
		liver	12.5	±16.5	4.20-27.6	4	
Overall Mean		muscle	0.47			51	
		liver	12.14			69	

[1] Number of fish analyzed above AAS detection limits.

[2] Liver/muscle ratio is the average from individual fish.

Table 26. Zinc and Copper in Benthic Insects and Sediments (mg/kg) from Anderson Lake. (Station 1 is at the inlet, Stations 2 and 3 were open water.)

Station	Aquatic Insects				Sediments
	Chironomidae	Libellulidae	Chaeborinae	Heleida	
Zinc					
2 (8/5/73)	147	---[1]	468	---	---
1 (8/20/73)	858	185	---	---	3250
2 (8/20/73)	216	---	538	---	3550
3 (8/20/73)	50	---	---	188	2150
Copper					
2 (8/5/73)	20	---	78	---	---
1 (8/20/73)	52	37	---	---	76
2 (8/20/73)	13	---	66	---	87
3 (8/20/73)	20	---	---	---	34

[1] Indicates not enough organisms collected for analysis.

pattern of decreasing metal concentrations at higher trophic levels. Chaoborus sp., on the other hand, which is predaceous on micro-crustacea and smaller insects, contained higher levels than the chironomids.

E. Lateral Lake Study Summary

The water in the lakes was uniform in chemical composition except for levels of Zn. Zinc concentrations were highest near the inlets from the river.

Zinc, Cu, Cd, Pb and Sb exceeded background levels in the sediments of the lakes. In general, the metals in the sediments decreased to a minimum at stations farthest removed from the river.

Yellow perch from a number of the lakes contained higher levels of Zn, Cu and Cd than fish from the Bells Lake control station located on the St. Joe River. The differences in the metal content of the fish appeared to be correlated with the lake's connection to the Coeur d'Alene River.

The levels of the metals in the five species of fishes were fairly similar. However, there appeared to be a higher concentration of Zn in the muscle tissues of bullheads (omnivores) than in the muscle tissues of largemouth bass (carnivores).

III. Coeur d'Alene Lake

A. Water Quality

In our Title I report to OWRR (B-044 WASH and B-015 IDA), the water quality of Coeur d'Alene Lake was given a great deal of emphasis. As previously stated in the introductory section, it was decided to concentrate on completing the sediment coring of the lake, measuring the amounts and types of metallic elements being concentrated in the upper constituents of the food chain--mainly the fish population of the Coeur d'Alene-Spokane River drainage--and investigating the productivity of the Coeur d'Alene and Spokane Rivers.

Physiochemical Conditions

Much the same conditions prevailed in the lake during the 1973-74 period as did during our previous study in 1971-72, as evidenced by routine sampling during coring operations. Thermal stratification occurred in areas over 10 m deep in the mid and northern regions of the lake by late June and continued until late October.

Prodigious blue-green algal growth (mainly Aphanizomenon flos-aquae) took place in the Chatcolet and Hidden Lake region (Figures 5 and 7) as well as in many of the northern bay regions during the late summer period (August 1973). During the period of high runoff in February 1973, considerable sediment was distributed throughout the lake by Plummer Creek and the St. Joe and Coeur d'Alene rivers. Record high runoff in January, February and May 1974 caused heavy additions of sediment to the lake at those times, especially by the Coeur d'Alene River.

The results of standard water chemistry tests made during the summer productivity period were within those ranges described in our earlier report. For gross evaluation of the lake water quality, the reader is referred to Appendix D, Table D-1. The lake outlet station was located in Coeur d'Alene lake proper--before it flows into the Spokane River--and thus reflects the overall water quality conditions in the lake as they existed during the study.

B. Sediment Core Samples

As previously mentioned in the text, the results of our first five cores have been given in OWRR Report B-044 WASH and B-015 IDA. Cores 6-11 were taken in a northerly direction from the Coeur d'Alene River delta toward the outlet of the Spokane River. Cores 12-15 were taken in the St. Joe River-Chatcolet Lake region and then northward toward the Coeur d'Alene River delta area. Cores A-L were begun in the Chatcolet region and also progressed northward to the outlet. Alphabetically designated cores were taken in the bay regions while the cores with numerical identifications were located centrally along the lengthwise axis of the lake. Figures 1 and 43 indicate the location of the coring stations.

Core 6 (70cm length)

Core 6 was retrieved equidistant from the east and west shorelines (.7 km off Bell's Bay) in 23.3 m of water.

Analysis of Core 6 indicated that the uppermost 19 cm of sediments contain very high levels of metals such as Zn, Mg, Pb, Fe, Cu, Cd in

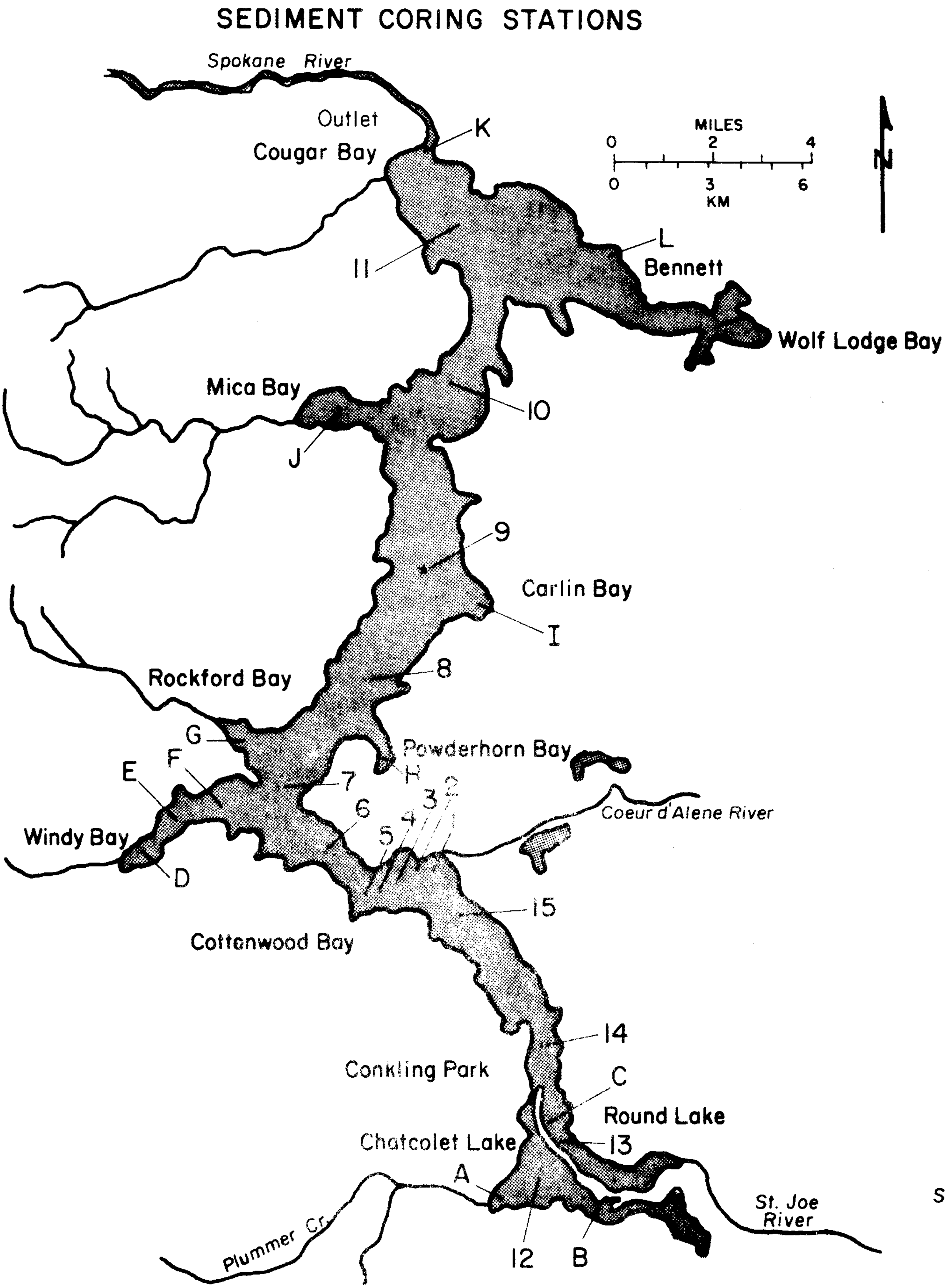

Figure 43. Coeur d'Alene Lake Coring Stations

comparison to sediments at lower levels. The shift to lesser amounts of metallics is fairly uniform, occurring for nearly all elements tested at the 15cm level.

Figures 44a and 44b show the metallic shifts as well as physico-chemical data.

Core 7 (70cm length)

Core 7 was taken equidistant from Rockford Point and East Point near the base of Windy Bay in 34m of water.

Core analysis indicates that the mining activities along the Coeur d'Alene River drainage area have resulted in the deposition of high levels of metallic sediments to an approximate depth of 10-20cm in this core.

All the metals (tested for) decline from high to relatively low values within a depth of 20cm from the surface, with the exception of Fe, which was found at high levels at the 25cm depth. Iron values also exhibited a peculiar drop at 11cm and then rose again at the 15-20cm sediment depth (Figure 45).

Core 8 (65cm length)

Core 8 was driven at a point midlake between Half Round Bay and Black Rock Bay in 44.2m of water. Core 8 is comparable to #7 to the extent that high levels of most of the metals analyzed for occur in the top 10cm of sediment; manganese shows an irregular trend. Additional analysis by neutron activation methods of this core indicated comparatively high levels (2.3-20.8 mg/kg) of Hg down to the 13cm level, but none of the other metals tested (Lu, Th, Cr, Hf, Ba, Ag, Zr,

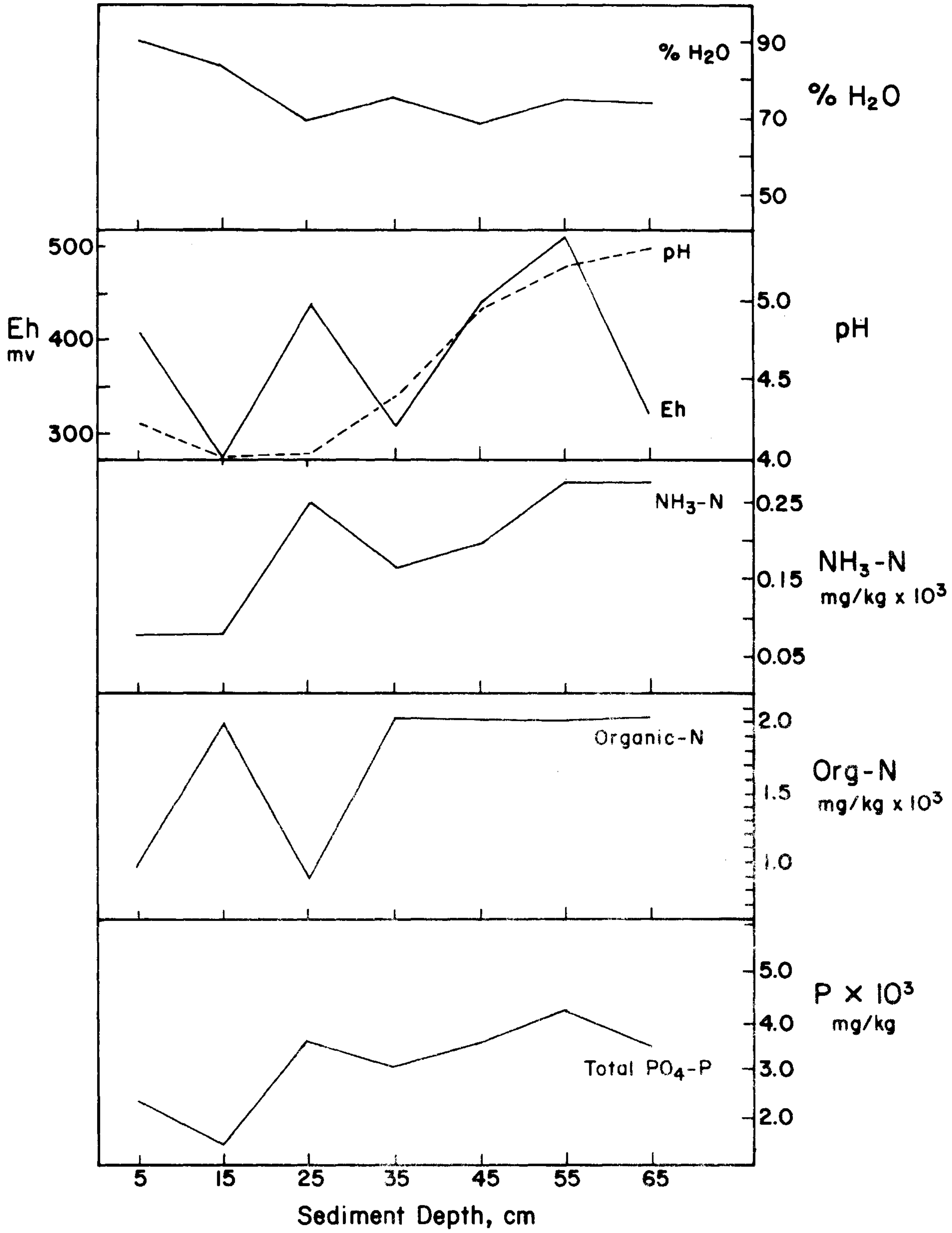

Figure 44(a). Standard Chemical and Atomic Absorption Analysis of Core 6 (.7km off Bell's Bay, 23.3m Water-depth).

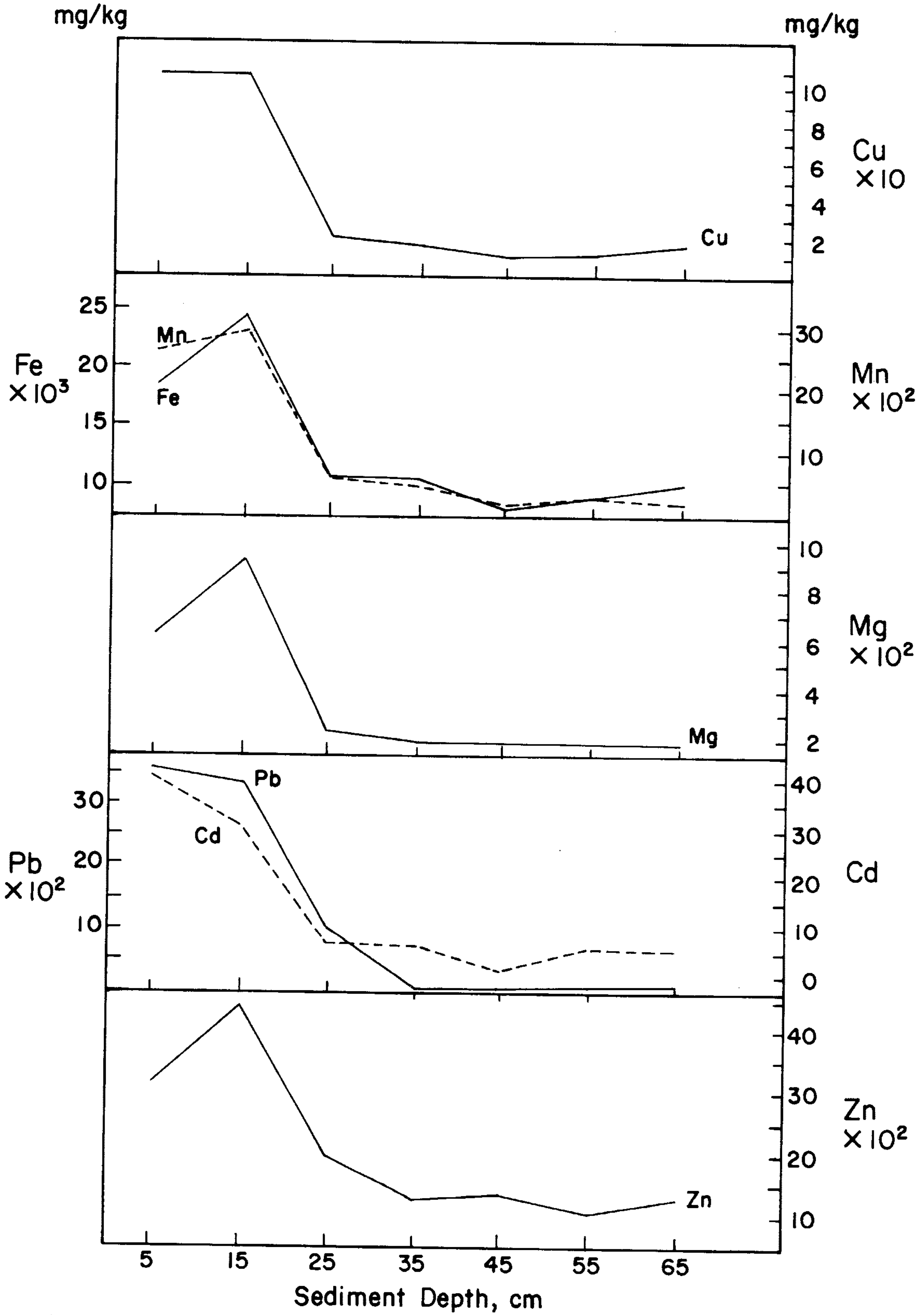

Figure 44(b). Atomic Absorption Analysis of Core 6 (.7 km off Bells Bay, 23.3 m Water-depth).

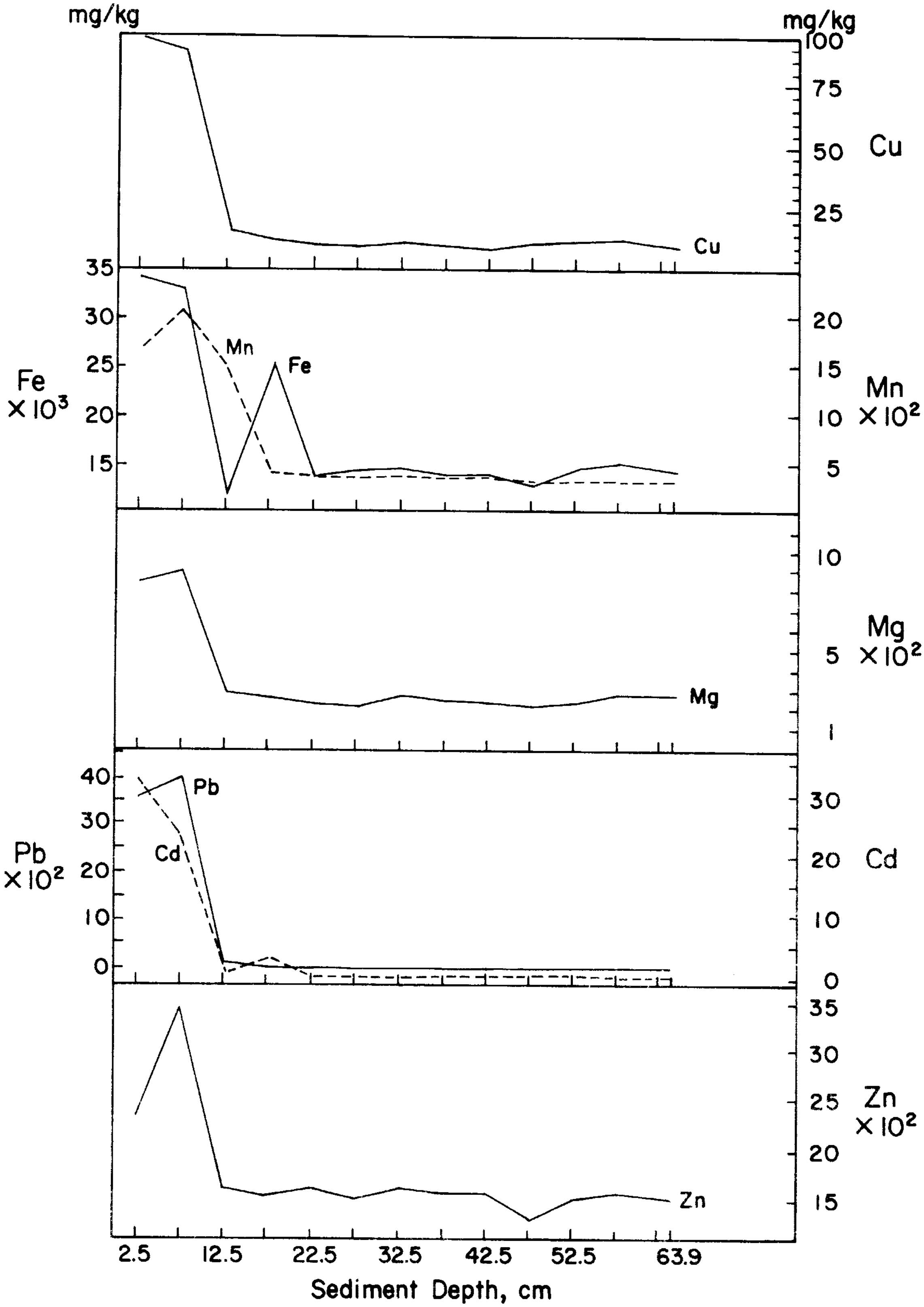

Figure 45. Atomic Absorption Analysis of Core 7 (Between Rockford Point and East Point, 34 m Water-depth).

Cs, Ni, Te, Sc, Rb, Fe, Zn, Ta, Co, Eu, Sb) exhibited an increase beyond the 10cm level (Figures 46a and 46b).

Core 9 (70cm length)

Core 9 was taken midlake, 1.2km off McDonald Point in 39.6m of water. Core 9 indicates a still thinner sediment segment containing higher levels of metallic elements. The metals (tested for) exceeded background level in the uppermost 0-8cm sediment layers. Manganese and zinc were also above background to 10-12cm depth. Core 9 was not graphed; data are presented in Appendix C, Table C-4.

Core 10 (108cm length)

Core 10 was taken in the midlake area between Twin Beaches and Echo Bay in 37.8m of water. The contents of this core were not analyzed, since two other cores were taken subsequently toward the lake outlet.

Core 11 (105cm length)

Core 11 was driven at a point equidistant between Tubbs Hill and Kidd Island, .9km off Tubbs Hill Light in 32.9m of water. Analyses by atomic absorption of Core 11 indicate that, of the metals tested, only Cd, Mg and Mn were found in significant amounts below the 5cm level (Figures 47a and 47b). Neutron activation analyses of subsamples revealed a similar trend. At the 5cm depth, neutron activation and atomic absorption Zn analyses approximate each other, being 3966 and 3948 mg/kg, respectively. Other metals tested for by activation analysis also showed comparatively higher levels in the upper sediment layers, such as Hg (3074 mg/kg), Cr (54 mg/kg), Ba (1154 mg/kg), Cs (16 mg/kg), Pb (170 mg/kg), Co (23 mg/kg)

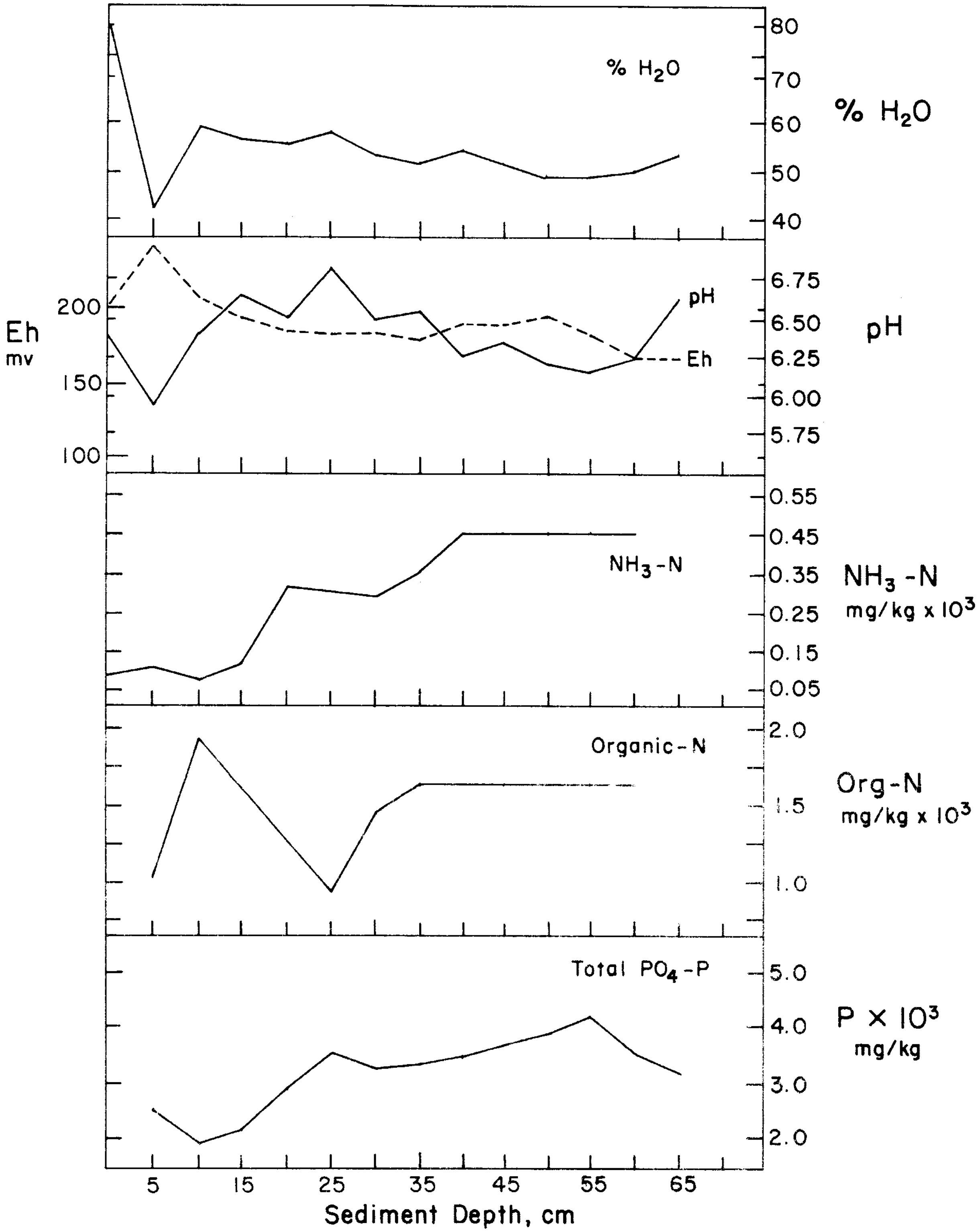

Figure 46(a). Standard Chemical and Atomic Absorption Analysis of Core 8 (Midpoint between Half Round and Black Rock Bays, 44.2m Water-depth).

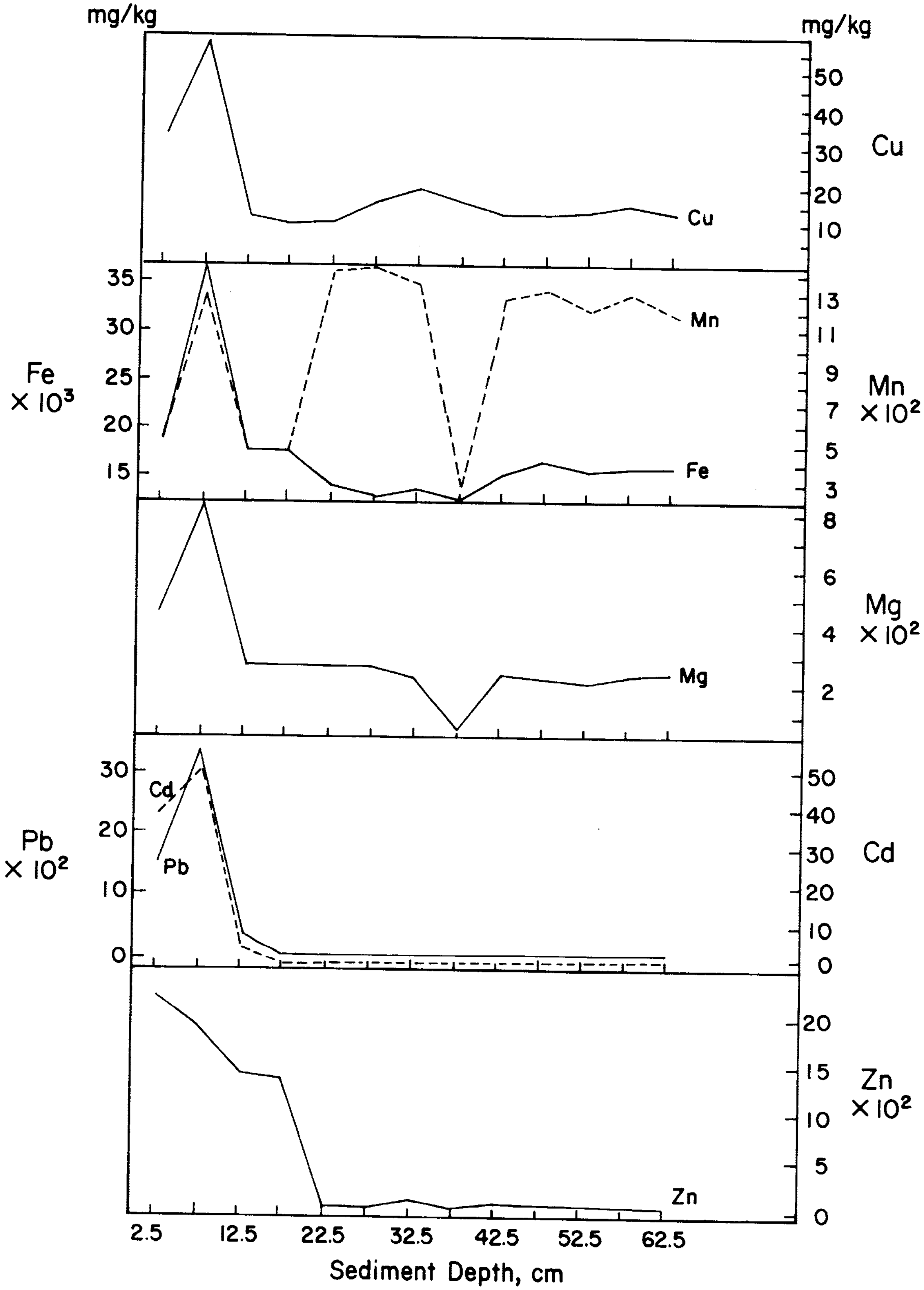

Figure 46(b). Atomic Absorption Analysis of Core 8 (Midpoint Between Half Round and Black Rock Bays, 44.2 m Water-depth).

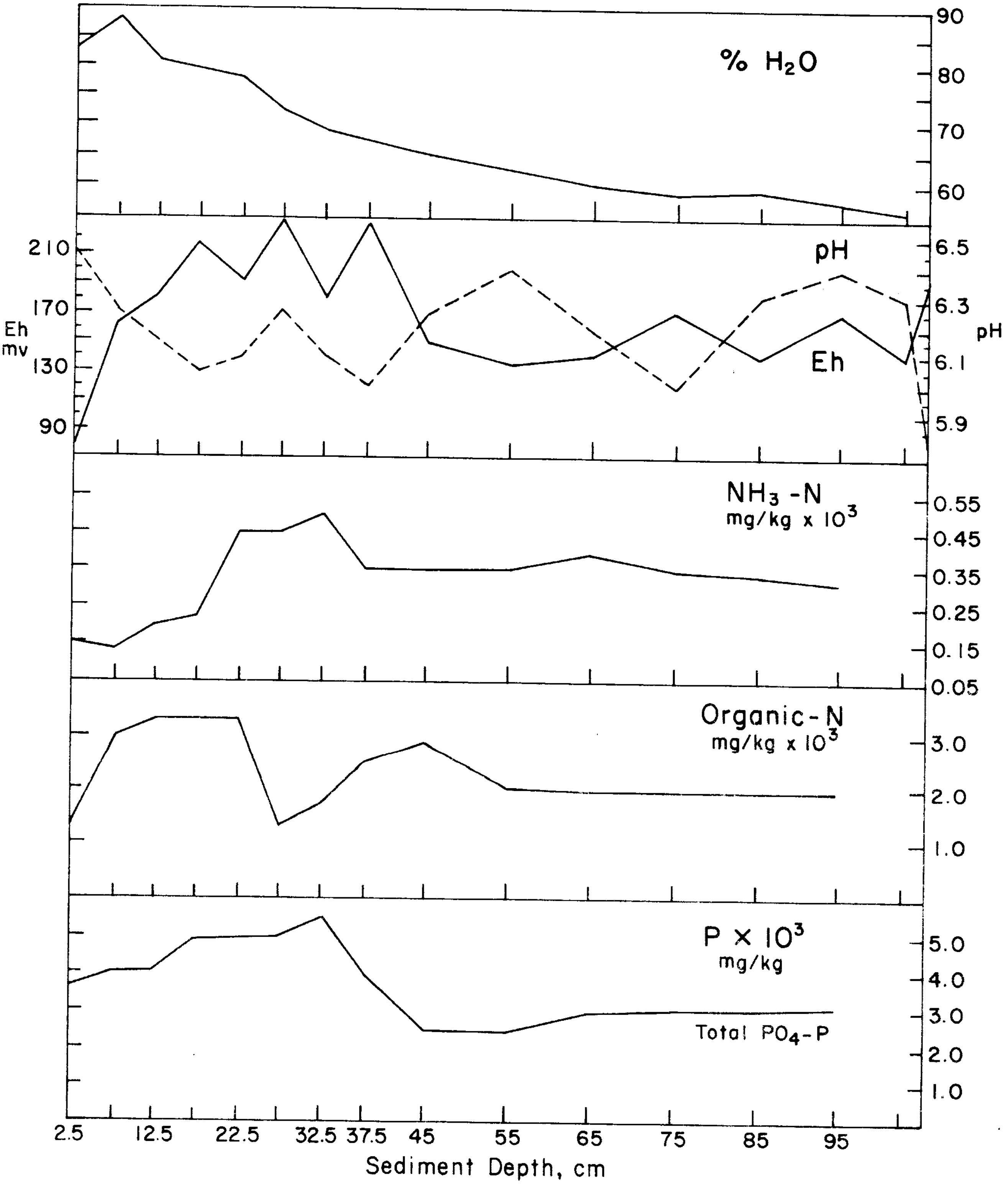

Figure 47(a). Standard Chemical and Atomic Absorption Analysis of Core 11 (.9km off Tubbs Hill Light, 32.9 m Water-depth).

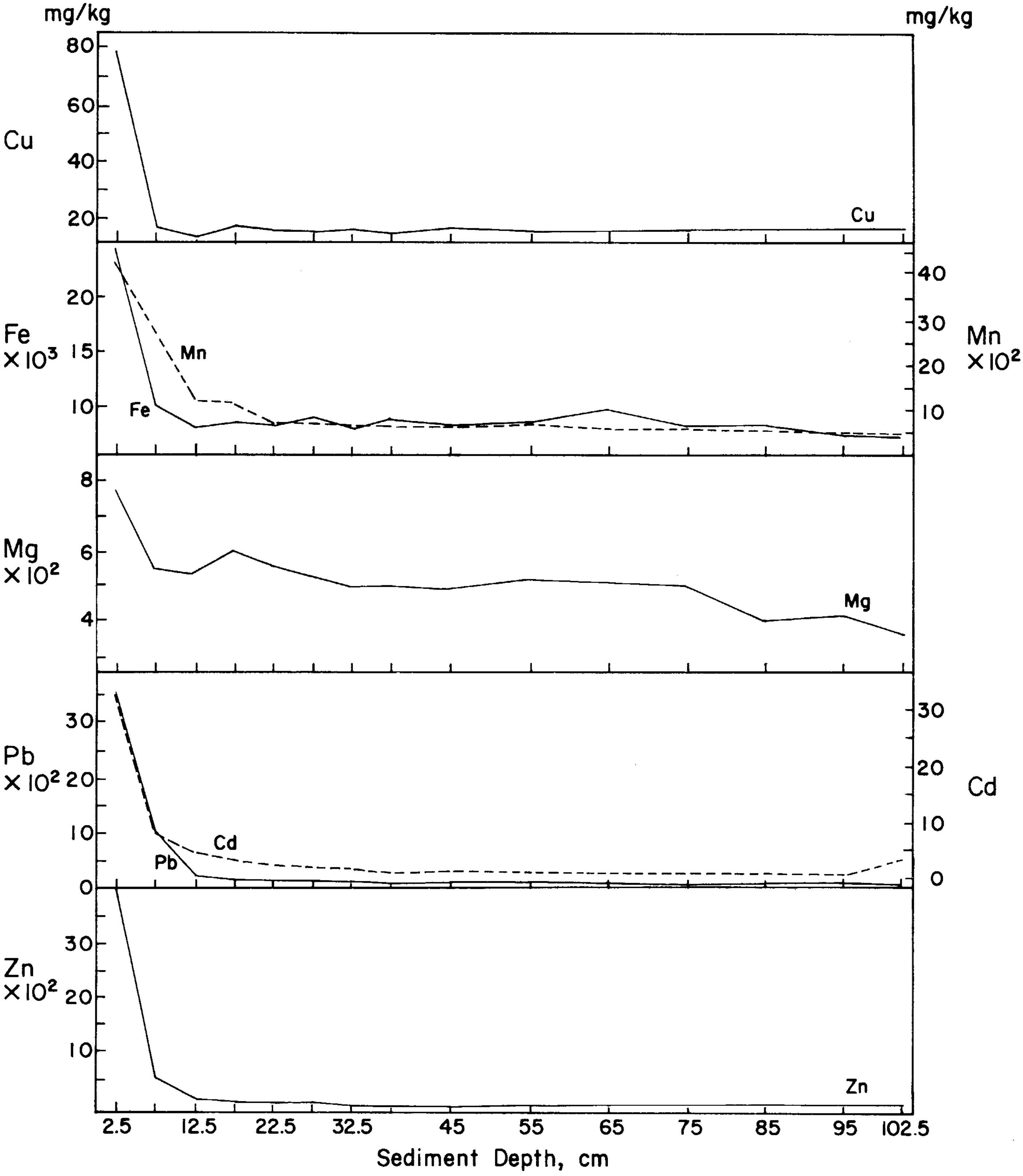

Figure 47(b). Atomic Absorption Analysis of Core 11 (.9 km off Tubbs Hill Light, 32.9 m Water-depth).

and Sb (72 mg/kg), especially in the upper 5cm sediment layers. These values were, in fact, two to four times the amount found below 5cm.

Core 12 (52cm length)

Core 12 was taken in the approximate center of the Chatcolet Lake area in 3m of water. Analysis by atomic absorption methods indicated no influence by the Coeur d'Alene River waters and relatively little influence by the St. Joe River. Subsample analysis of the metal content of the core indicated higher levels of Fe, Pb and Cd in the upper 5 to 7 cm of sediments. Other metals (tested for) did not reveal a consistent trend (Figure 48).

Core 13 (39cm length)

Core 13 was retrieved in 7.6m of water in the midchannel of the St. Joe River. This core exhibited slightly higher Zn, Pb and Cd levels in the upper 0-10cm layers. Manganese, Mg and Fe were also higher in these sediments than in the lower layers. Lead was comparatively higher down to the 23cm level. It is thought that human activity--possibly upstream manipulation of timber lands, agricultural practices and sewage disposal--may have influenced the type of metallic deposition in the sediments over the past 80-100 years (Figures 49a and 49b). Spooner (1973) and Skimp, Leland and White (1970) also have noted similar increases in the upper layers of cored sediments of lakes and related significant rises above background metallic elements such as Zn, K, Mn, Cr and Pb where human activity in watersheds has occurred.

Core 14 (43cm length)

Core 14 was driven at midpoint between Conkling Park and the eastern shoreline (.4km off Conkling Park) in 36.6m of water. Core 14

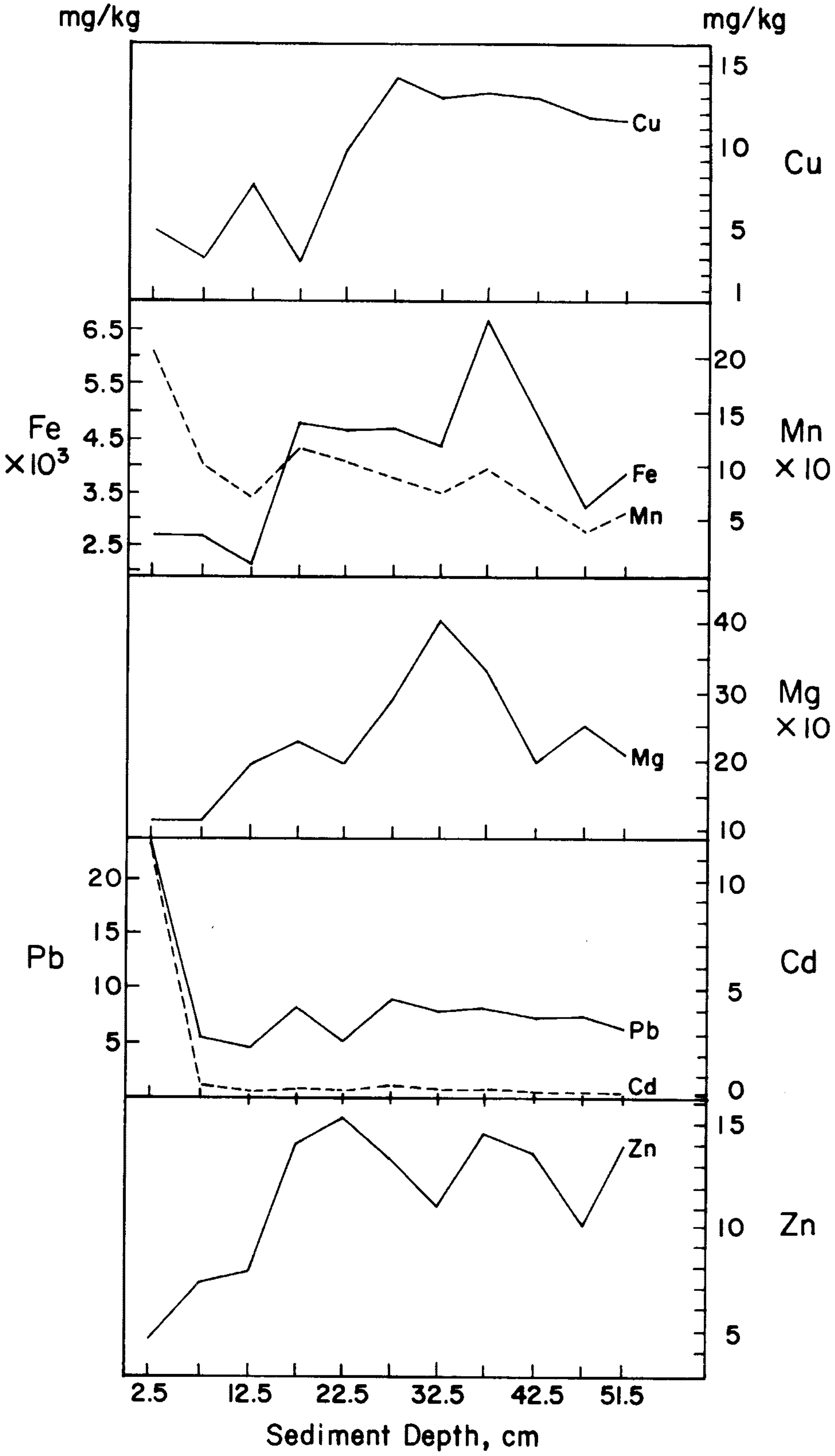

Figure 48. Atomic Absorption Analysis of Core 12 (Midpoint of Chatcolet Lake, 3m Water-depth).

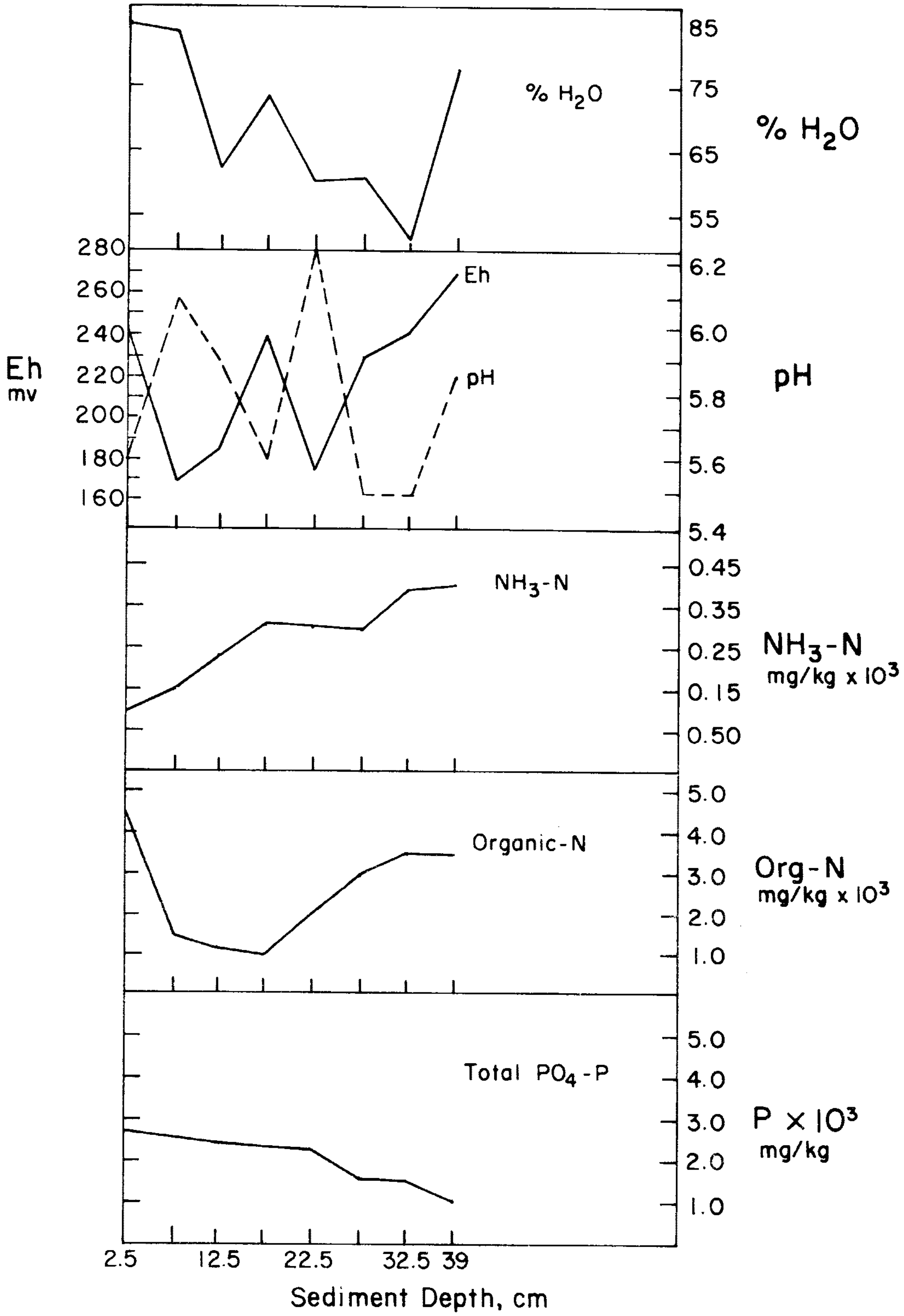

Figure 49(a). Standard Chemical and Atomic Absorption Analysis of Core 13 (Mid-channel, St. Joe River, 7.6m Water-depth).

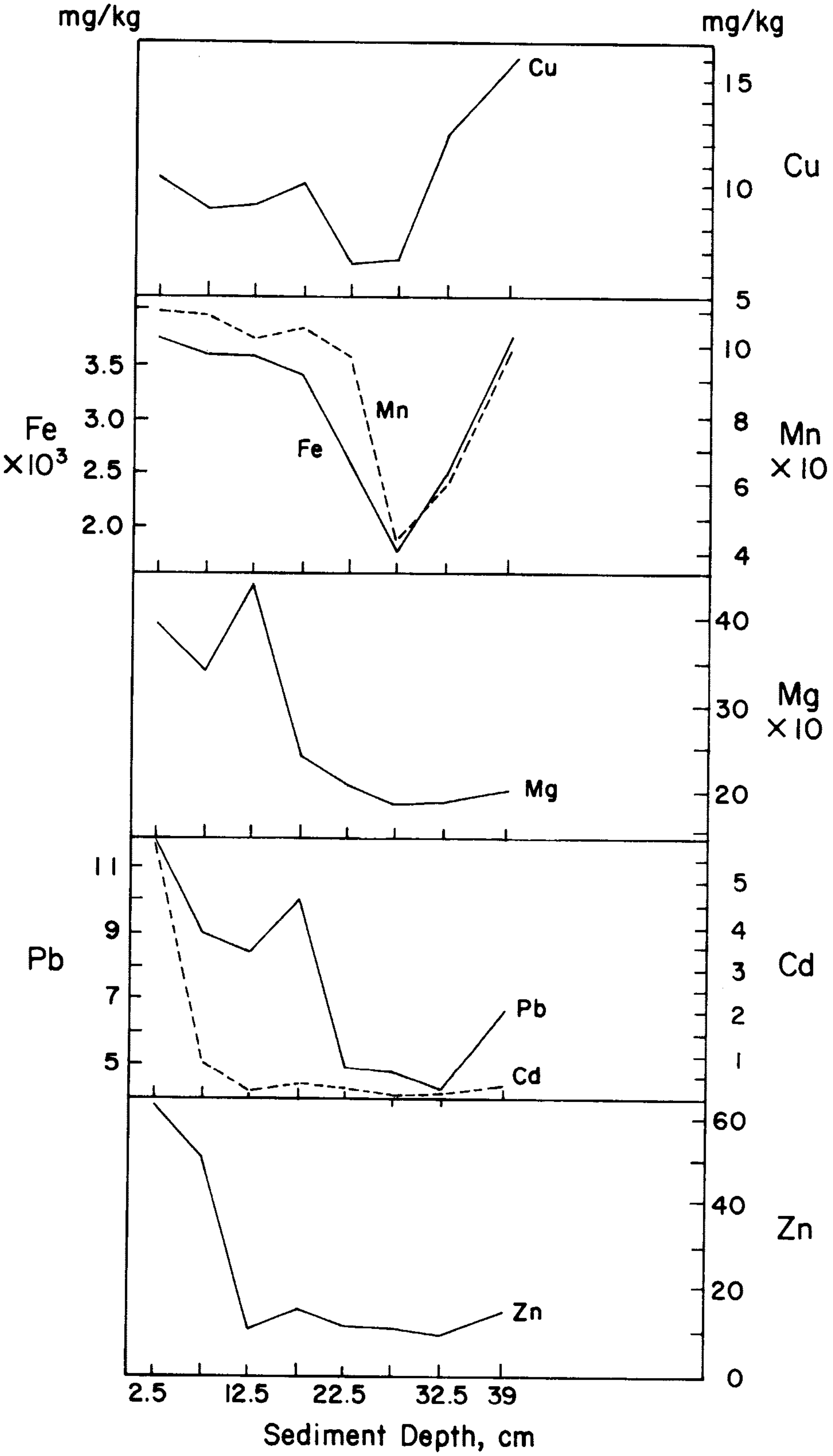

Figure 49(b). Atomic Absorption Analysis of Core 13 (Mid-channel St. Joe River in 7.6 m Water-depth).

shows a higher-than-background level of metallic elements. Zinc is present in amounts two to three times higher in 15 to 25cm levels than in the lower sediment layers. Other metals (tested for) are also higher at the same depths but most show an erratic pattern. This core was driven at a point 6.0km south of the mouth of the Coeur d'Alene River and, while the river flow is to the north, it is quite apparent that some constituents have moved in a southerly direction. Wind action and lake circulation probably are responsible for this distribution. The values, although higher than background, are still greatly reduced over those in the Coeur d'Alene River delta and the northern coring stations (Figures 50a and 50b).

Core 15 (72cm length)

Core 15 was not analyzed, because of the close proximity of some of our earlier dredge and grab samples (OWRR B-044 WASH and B-015 IDA). It was found in the previous work that the top 5cm of sediment from this area carried very high amounts of Zn (3000-3500 mg/kg) and Pb (3000-3100 mg/kg). These levels indicate a strong influence of the Coeur d'Alene River at least 3km south of the river mouth. It is postulated that a sharp decline in the metal load of the sediments occurs between this coring station and the station off Conkling Park (Core 14).

Core A (35cm length)

Core A was taken in the Plummer Creek delta region .215km off the west shore in 3m of water. Core A indicates very little difference in levels of metallic elements tested throughout its length. Zinc, Cu and Cr were within those amounts considered as usually present (Bowen, 1966; Canney, 1959). Lead was not detectable (Figure 51).

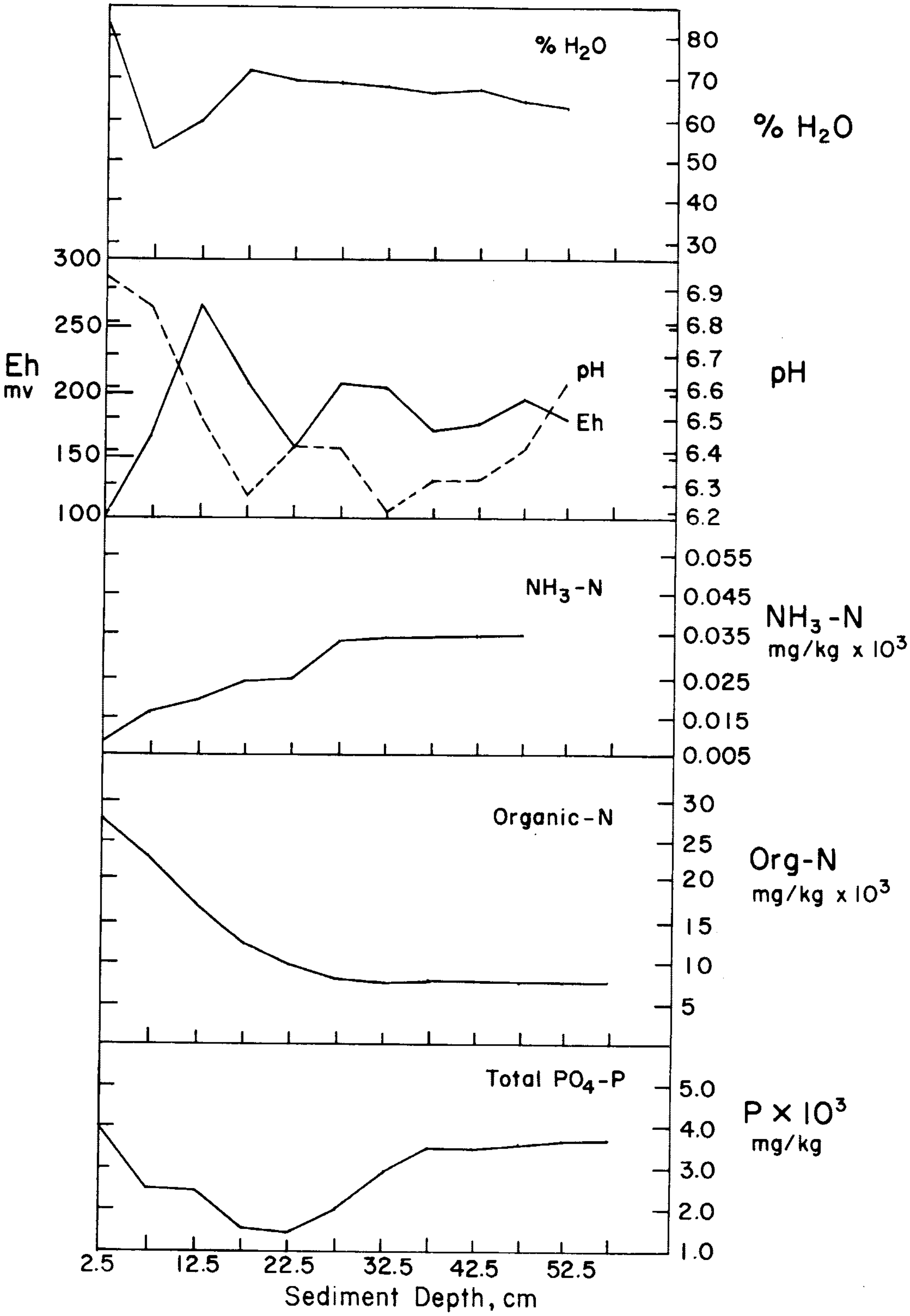

Figure 50(a). Standard Chemical and Atomic Absorption Analysis of Core 14 (.4km off Conkling Park, 36.6m Water-depth).

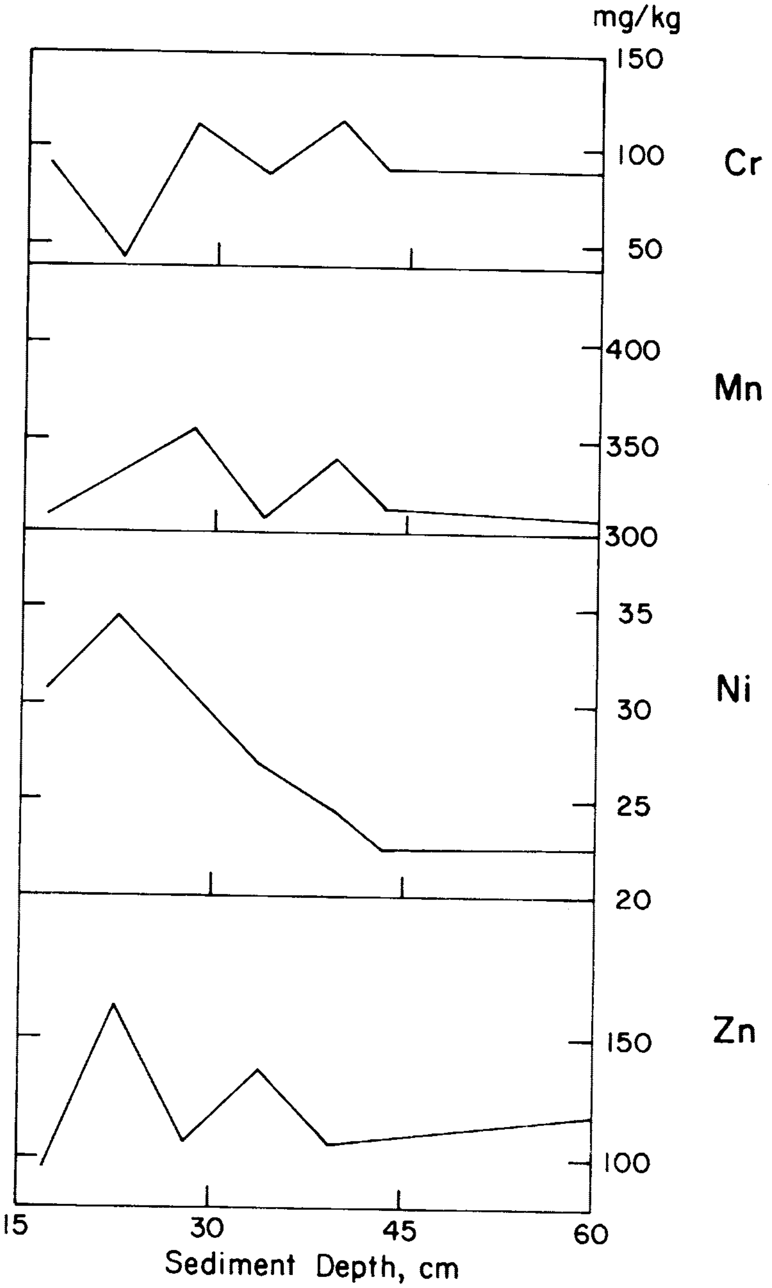

Figure 50(b). Atomic Absorption Analysis of Core 14 (.4 km off Conkling Park, 36.6 m Water-depth).

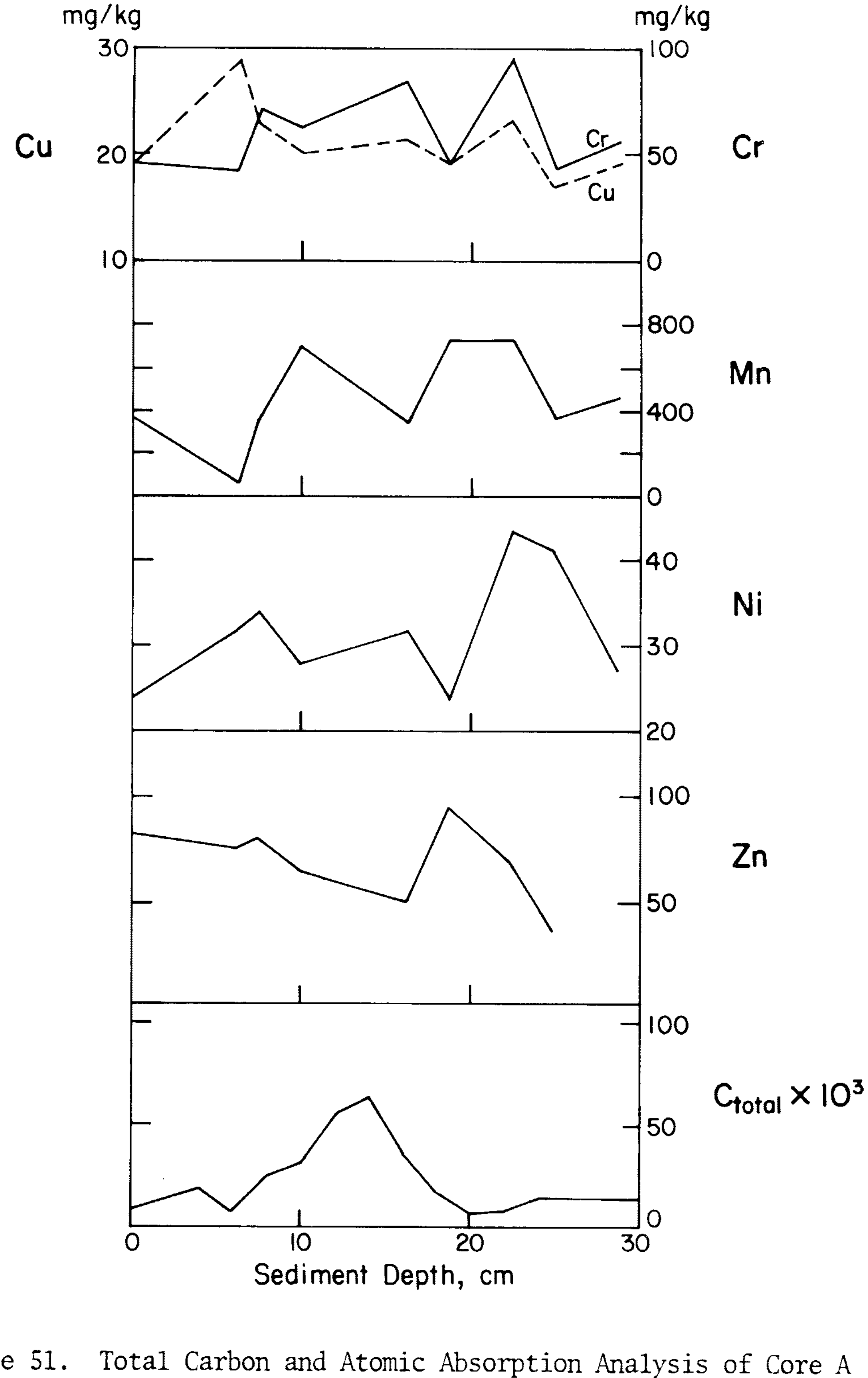

Figure 51. Total Carbon and Atomic Absorption Analysis of Core A (.215km off West Shore, Plummer Creek Delta, 3m Water-depth).

Core B (53cm length)

Core B was obtained .53 km north of Idaho State Highway 5 in the eastern area of Chatcolet Lake in 3 m of water. The flow of metallic elements from the Coeur d'Alene River does not appear to have progressed southward to this core site. Measurement of the sediment layers from 15 to the 52cm depth did not reveal higher levels of Zn, Pb and Cu than those considered to be naturally present in the soils of the area. Lead at the 0 to 15cm levels was considerably higher than background (Figures 52a and 52b).

Core C (60cm length)

Core C was driven at the mouth of the St. Joe River 1.28 km east of Chatcolet Park. There is some evidence that higher than average amounts of Zn and Pb are present in this area. The 0-2cm levels indicate about twice that amount expected to be present, while the lower sediment layers are well within ambient limits. It is thought that the higher amounts of these metals are probably the result of human activities in the St. Joe region rather than the result of mining activity in the Coeur d'Alene drainage. Spooner (1973) has cited evidence of this phenomenon in his study on central Michigan lakes (OWRR-A-066-MICH). Data for core C are shown in Figures 53a and 53b.

Core D (65cm length)

Core D was obtained in 7.6 m of water 1.21 km out from the mouth of Lake Creek in Windy Bay. This core showed a relatively small rise in Cr, Mn, Pb and Zn over background--down to the 7-12cm level. This coring station was 4.42 km from the mouth of the bay and is relatively

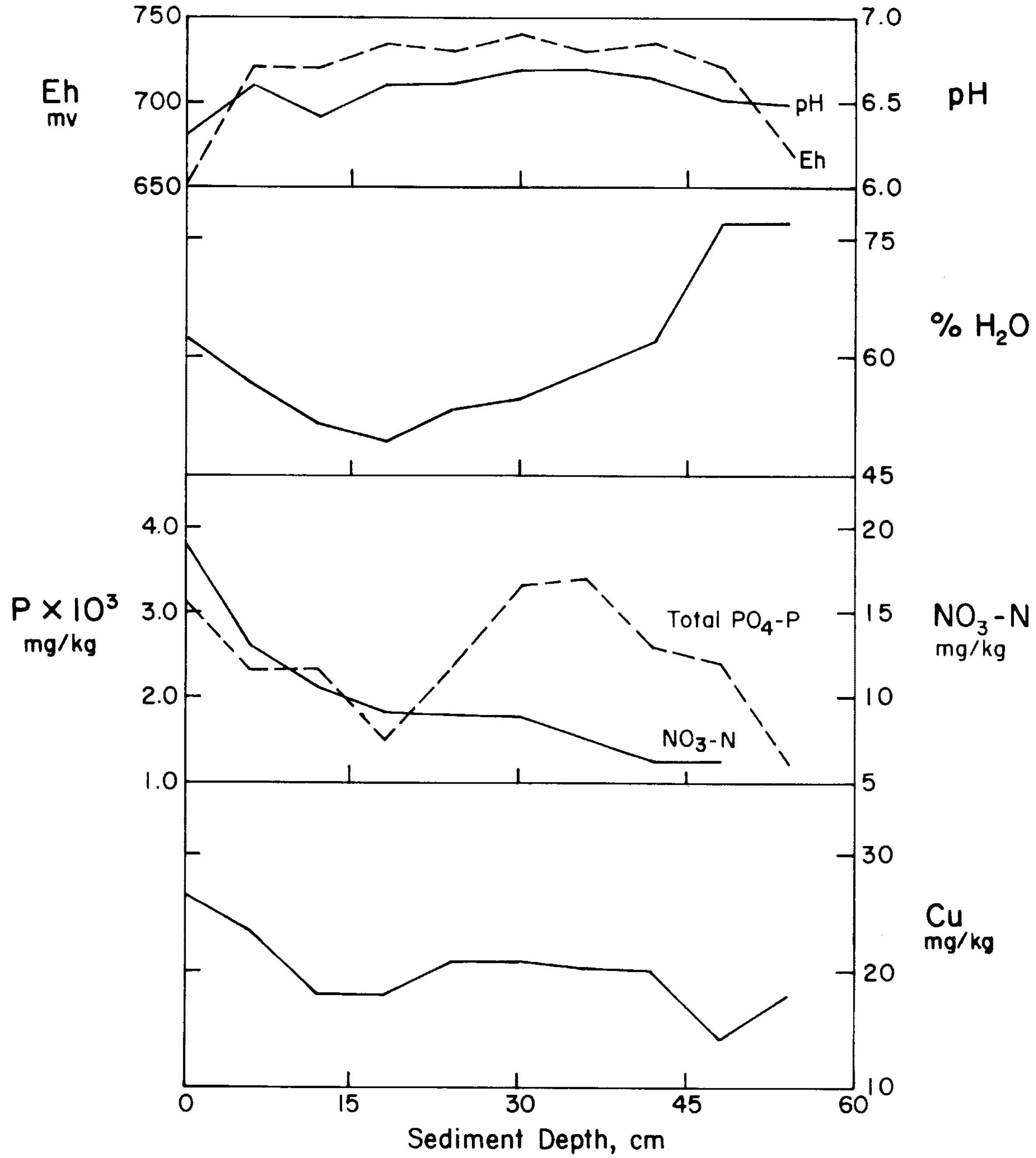

Figure 52(a). Standard Chemical and Atomic Absorption Analysis of Core B (Eastern area of Chatcolet Lake, 3m Water-depth).

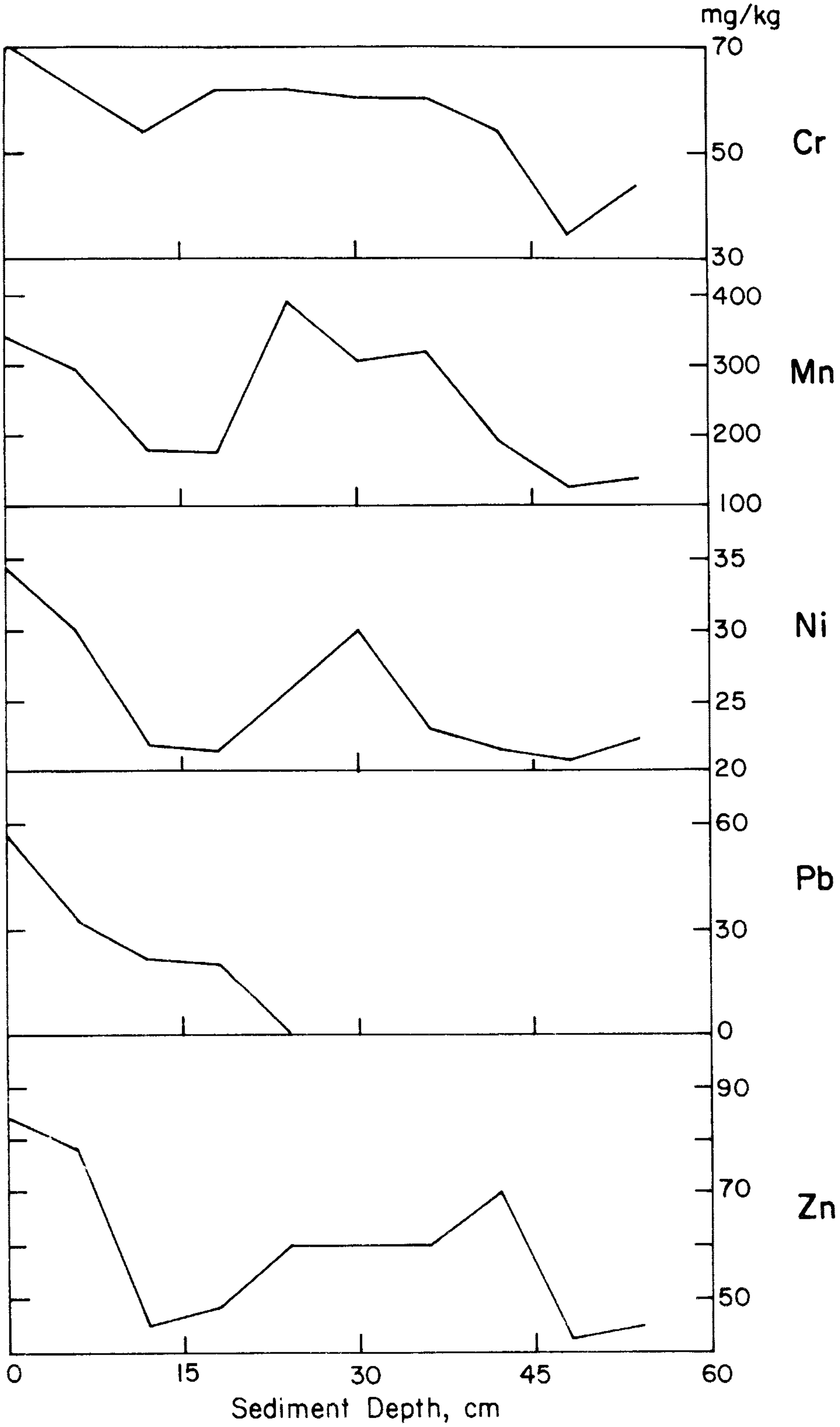

Figure 52(b). Atomic Absorption Analysis of Core B (Eastern Area of Chatcolet Lake, 3 m Water-depth).

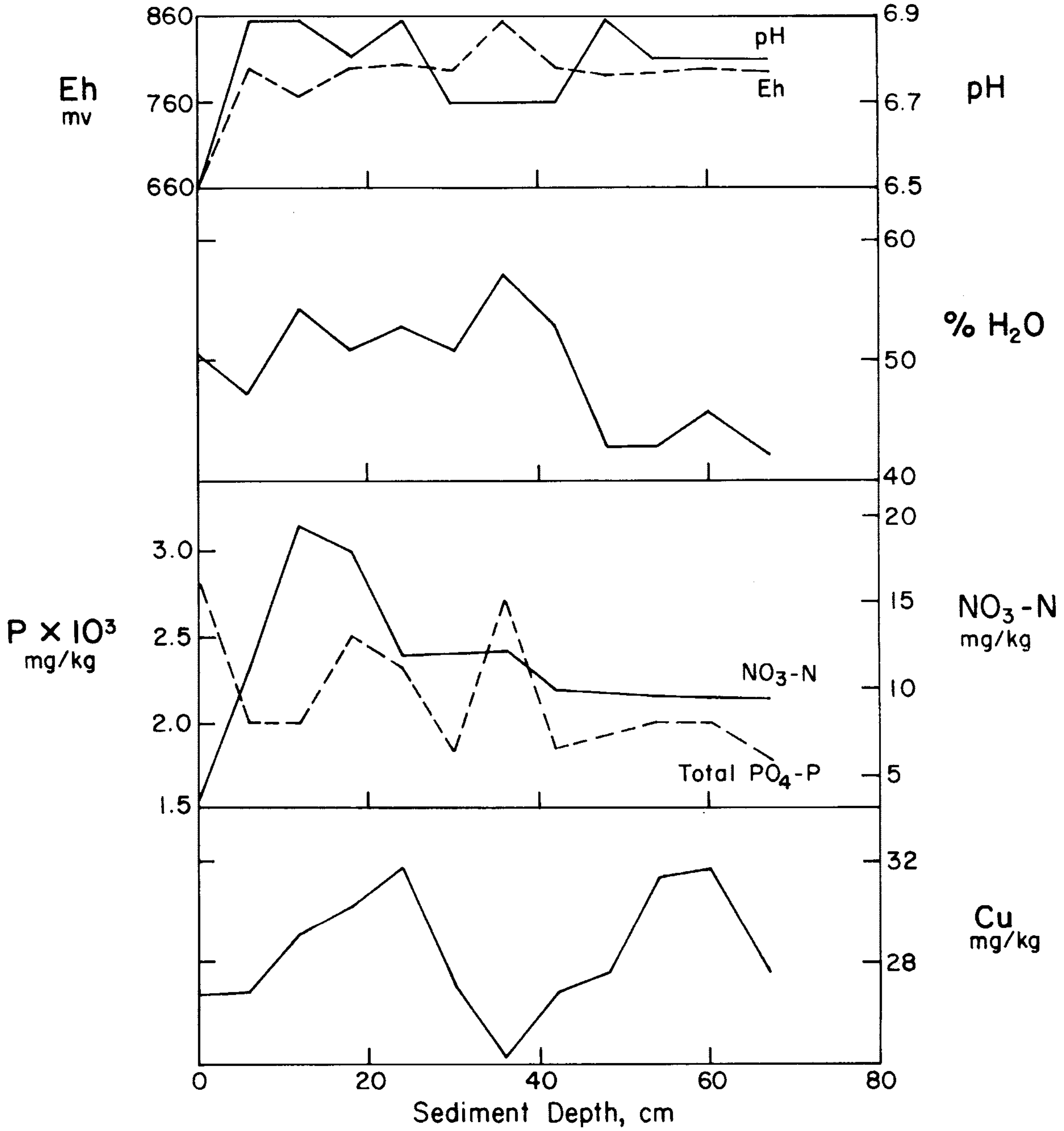

Figure 53(a). Standard Chemical and Atomic Absorption Analysis of Core C (Mouth of St. Joe River, 7.6m Water-depth).

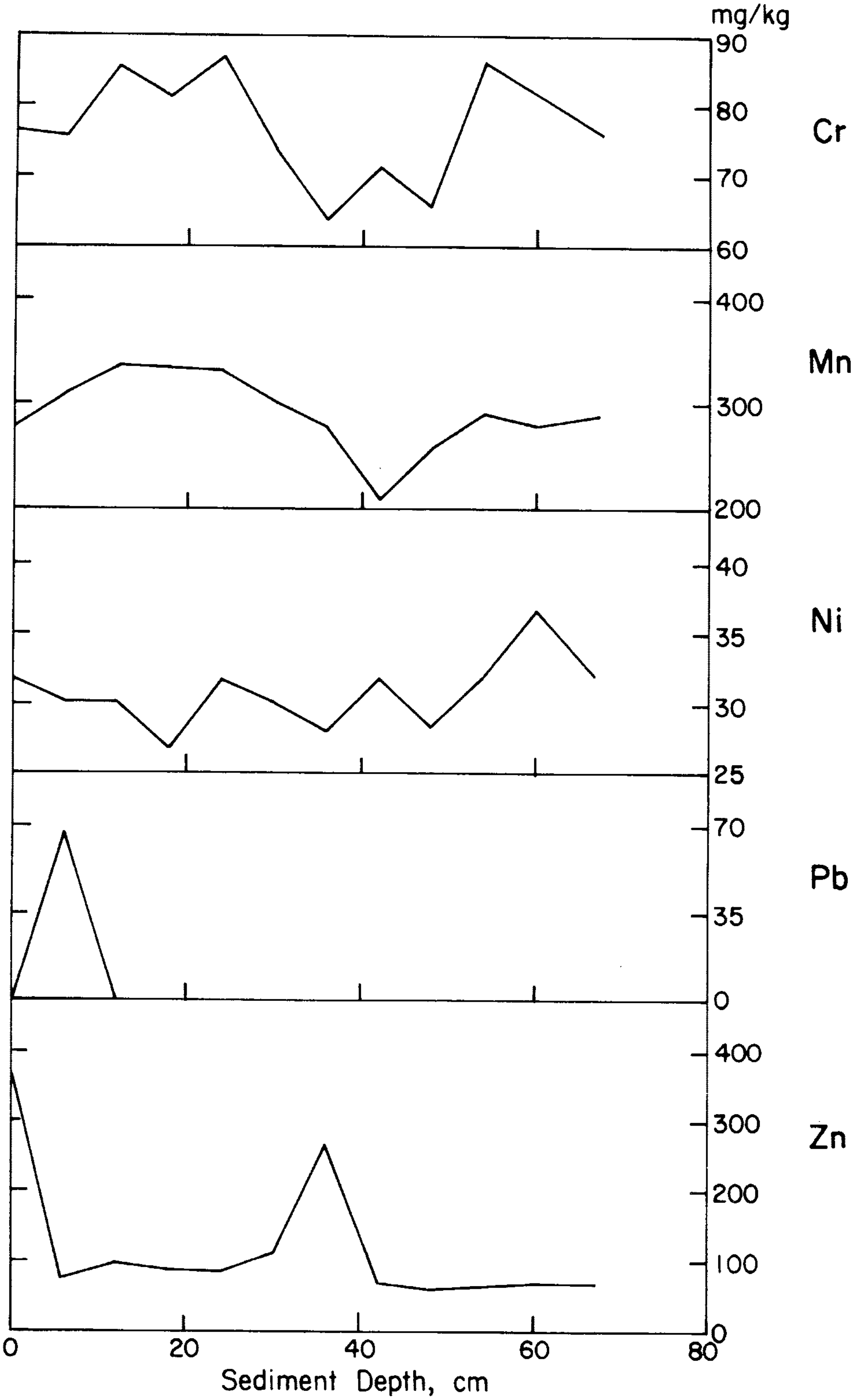

Figure 53(b). Atomic Absorption Analysis of Core C (Mouth of St. Joe River, 7.6 m Water-depth).

sheltered from the main lake body. Lake Creek and other small tributaries also may have had an effect in diluting and preventing additional entrance of metallic pollutants that far up the bay. The data for this core are not graphed.

Core E (60cm length)

Core E was taken in 10 m of water 3.2 km from the entrance of Lake Creek and toward the mouth of Windy Bay. This core shows very high levels of Pb, Zn, Cu and Cr down to the 12cm level. Sediments analyzed below this level are slightly above those expected in surrounding soils (Figures 54a and 54b).

Core F (58cm length)

The contents of Core F were not analyzed. However, Core 7 was taken in the same general area as Core E which, as previously stated, contained high levels of Pb, Zn and Cr down to the 10cm level.

Core G (54cm length)

Core G was driven in Rockford Bay 1.8 km from Rockford Creek in 8 m of water. The sediments in the upper 6 cm were somewhat lower in heavy metal content than were the sediments between the 8 to 18cm layers. Most likely these lower values in the overlying sediments are due to the mixing of eroded soils from the drainage immediately around Rockford Bay with the metal-laden waters entering the bay from the lake proper, (Figures 55a and 55b).

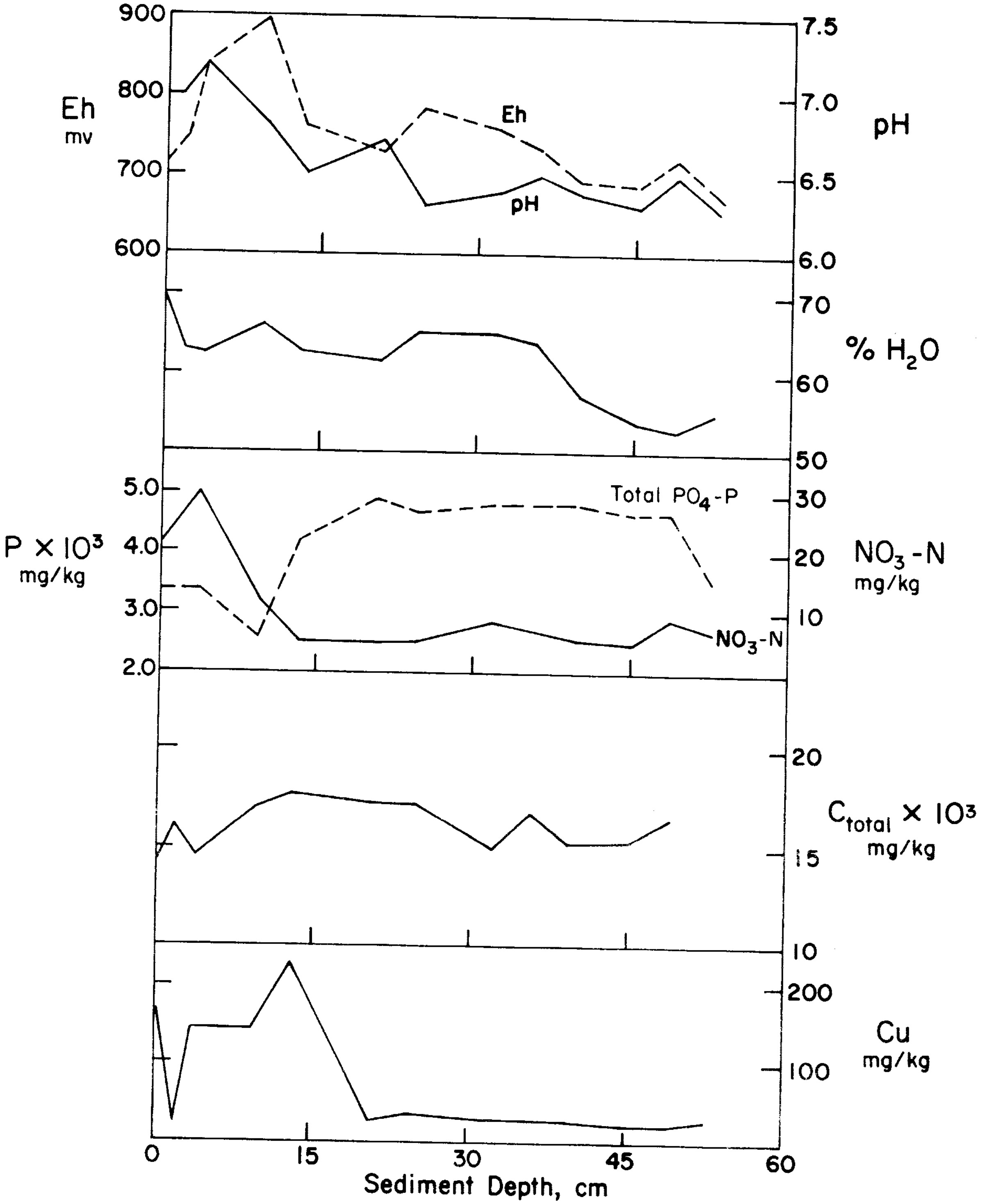

Figure 54(a). Standard Chemical, Total Carbon and Atomic Absorption Analysis of Core E (3.2km from Mouth of Lake Creek, 10m Water-depth).

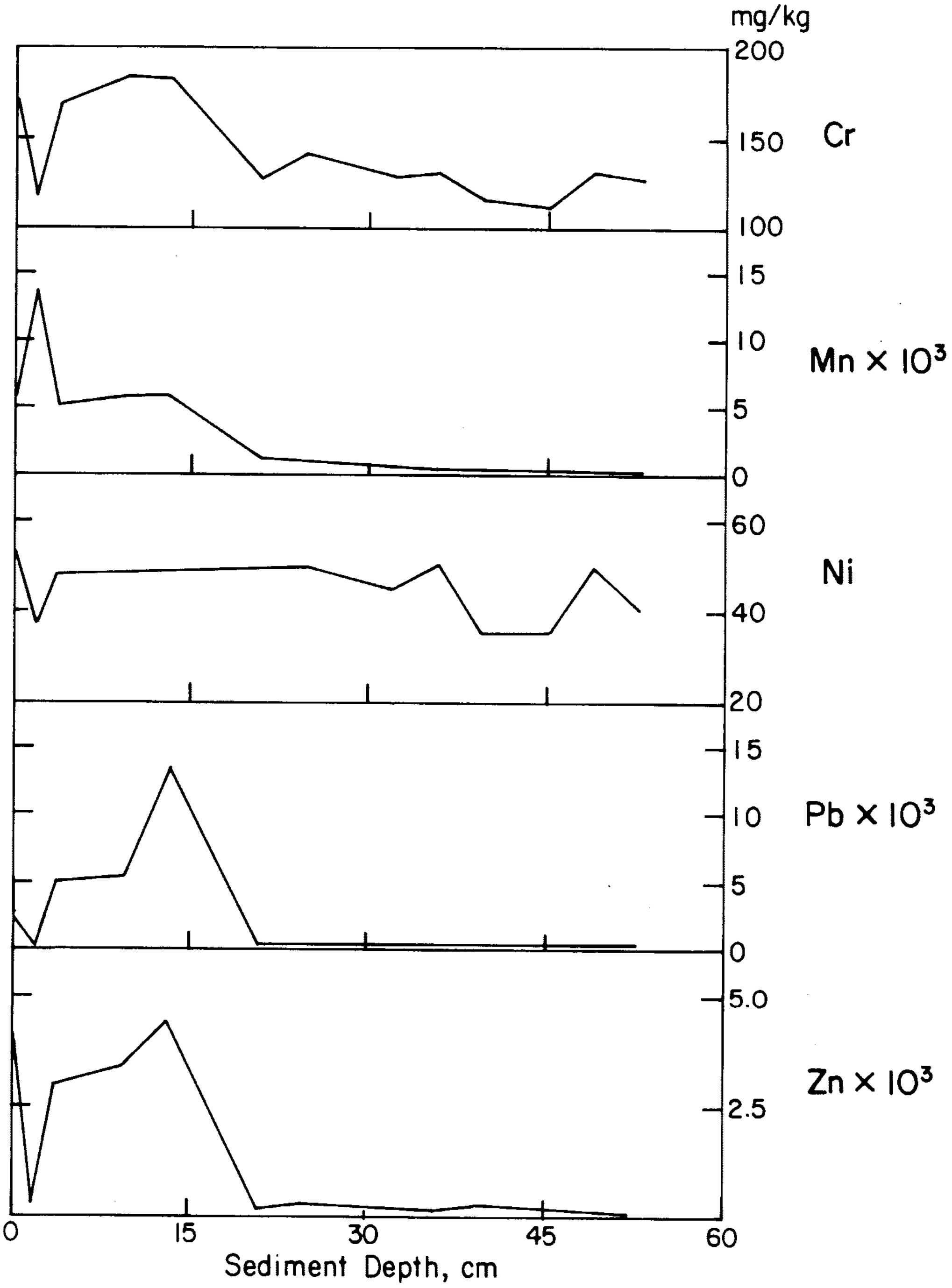

Figure 54(b). Atomic Absorption Analysis of Core E (3.2 km from Mouth of Lake Creek, 10 m Water-depth).

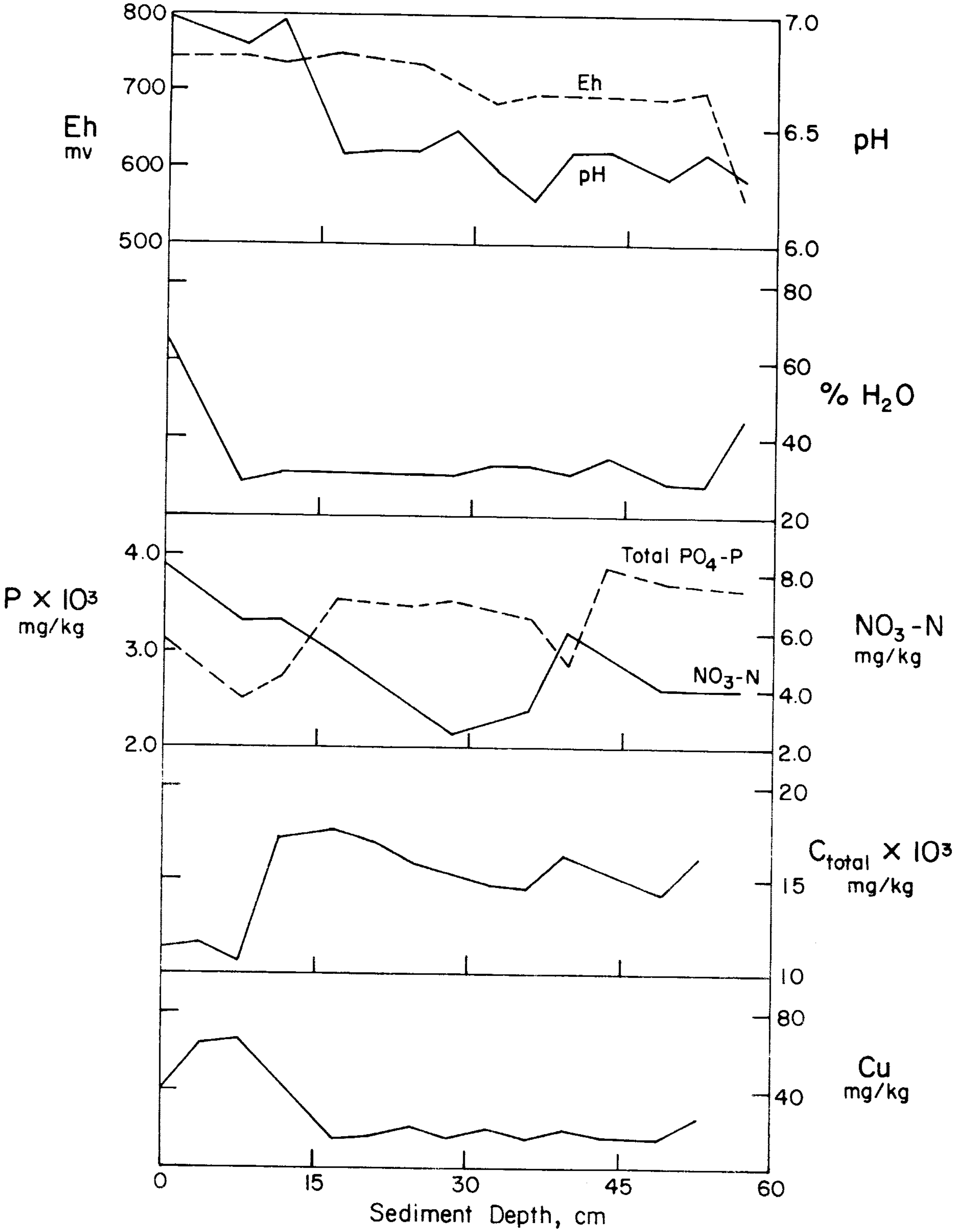

Figure 55(a). Standard Chemical, Total Carbon and Atomic Analysis of Core G (Rockford Bay, 1.8km From the Mouth of Rockford Creek, 8m Water-depth).

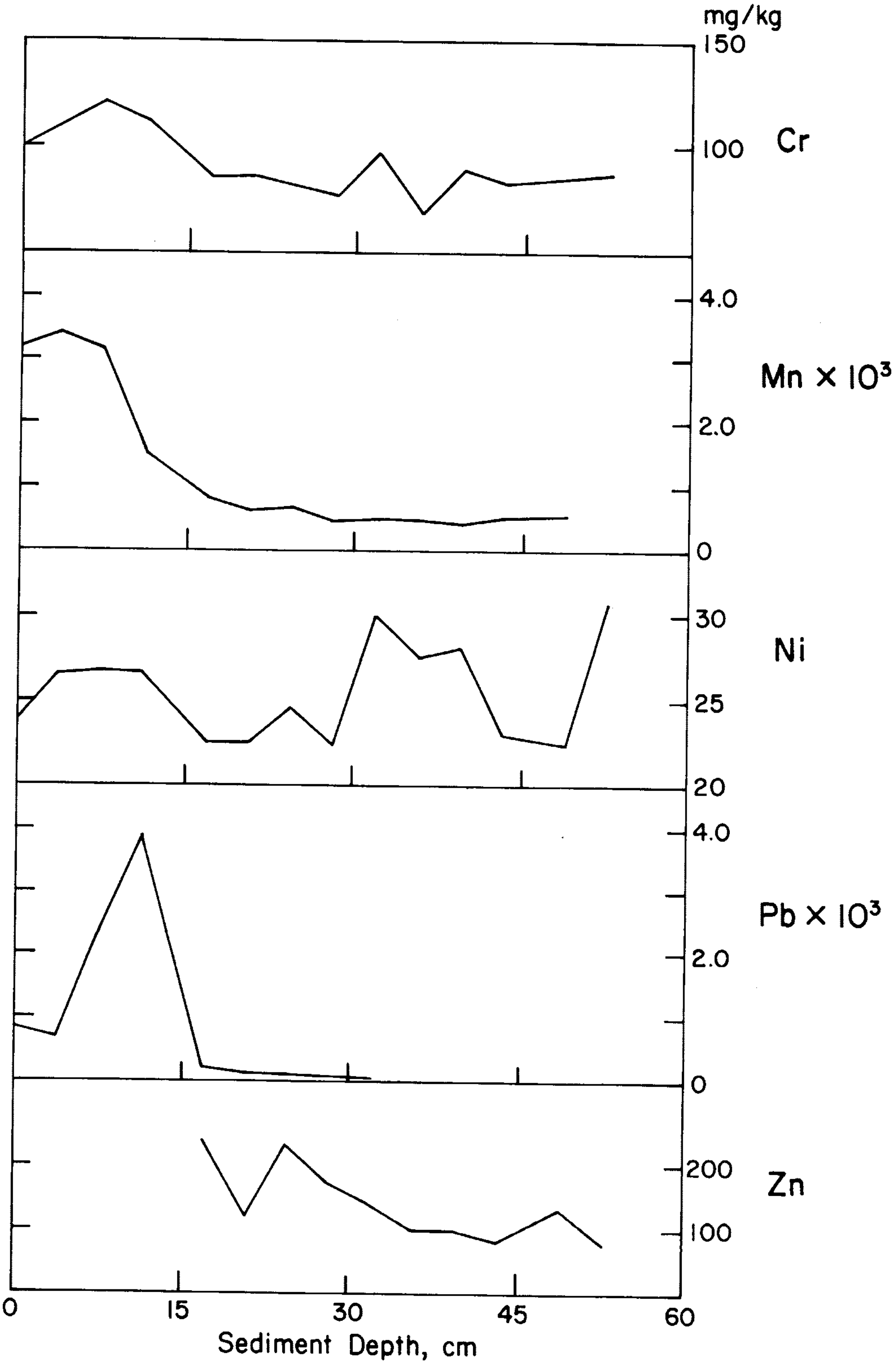

Figure 55(b). Atomic Absorption Analysis of Core G (Rockford Bay, 1.8 km From the Mouth of Rockford Creek, 8 m Water-depth).

Core H (45cm length)

Core H was retrieved from midpoint (1.3 km from Tributary Creek) of Powderhorn Bay on the east side of Coeur d'Alene Lake in 8 m of water. Core H indicated very high levels of certain metals (Pb, Zn, Cu, Cd and Cr) in the upper 15cm layers. It was interesting to note that values increased from the surface down to a maximum at the 15-19cm level and then declined to background levels from the 19 to the 45cm depth. One reason for the higher content of metals in this area may be the flow of the Coeur d'Alene River through the lake passing close to the mouth of this bay--as evidenced by muds carried by spring runoff (Figures 56a and 56b).

Core I (51cm length)

Core I was taken in Carlin Bay .4 km outward from the mouth of Carlin Creek in 7 m of water. This station is located in a relatively sheltered area of the lake; however, high levels of several metallic constituents of the sediments (Cu, Pb, Mn, Ni and Zn) were found in the first 0-3 cm of sediments. In lower sediment levels--down to the 51cm depth--the metallic content is at background levels (Figures 57a and 57b). Activation analysis of another core at the same location confirmed these results and, surprisingly enough, both the atomic absorption and activation analysis of Zn content were within 1% of each other in the upper layers. Other elements tested (Lu, Hg, Th, Cr, Hr, Ba, Ag, Zr, Cs, Ni, Tb, Sc, Rb, Fe, Ta, Co, Eu and Se) were 20 to 1000% higher in the upper 2cm sediment layers. Hg was 2.9 mg/kg at the 0-2cm layers but was no higher than .22 mg/kg at greater depth.

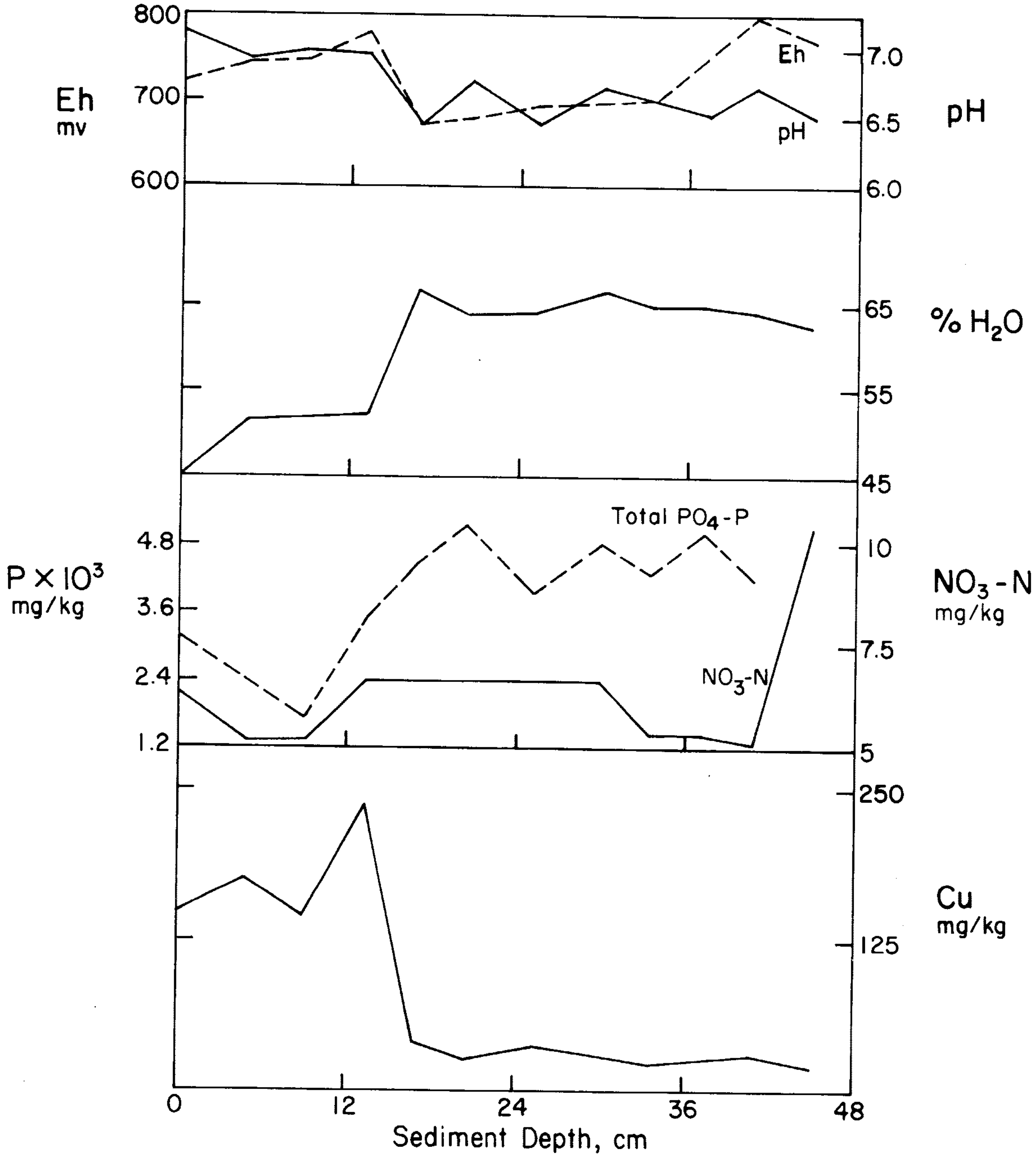

Figure 56(a). Standard Chemical and Atomic Absorption Analysis of Core H (1.3km from Tributary Creek, 8m Water-depth).

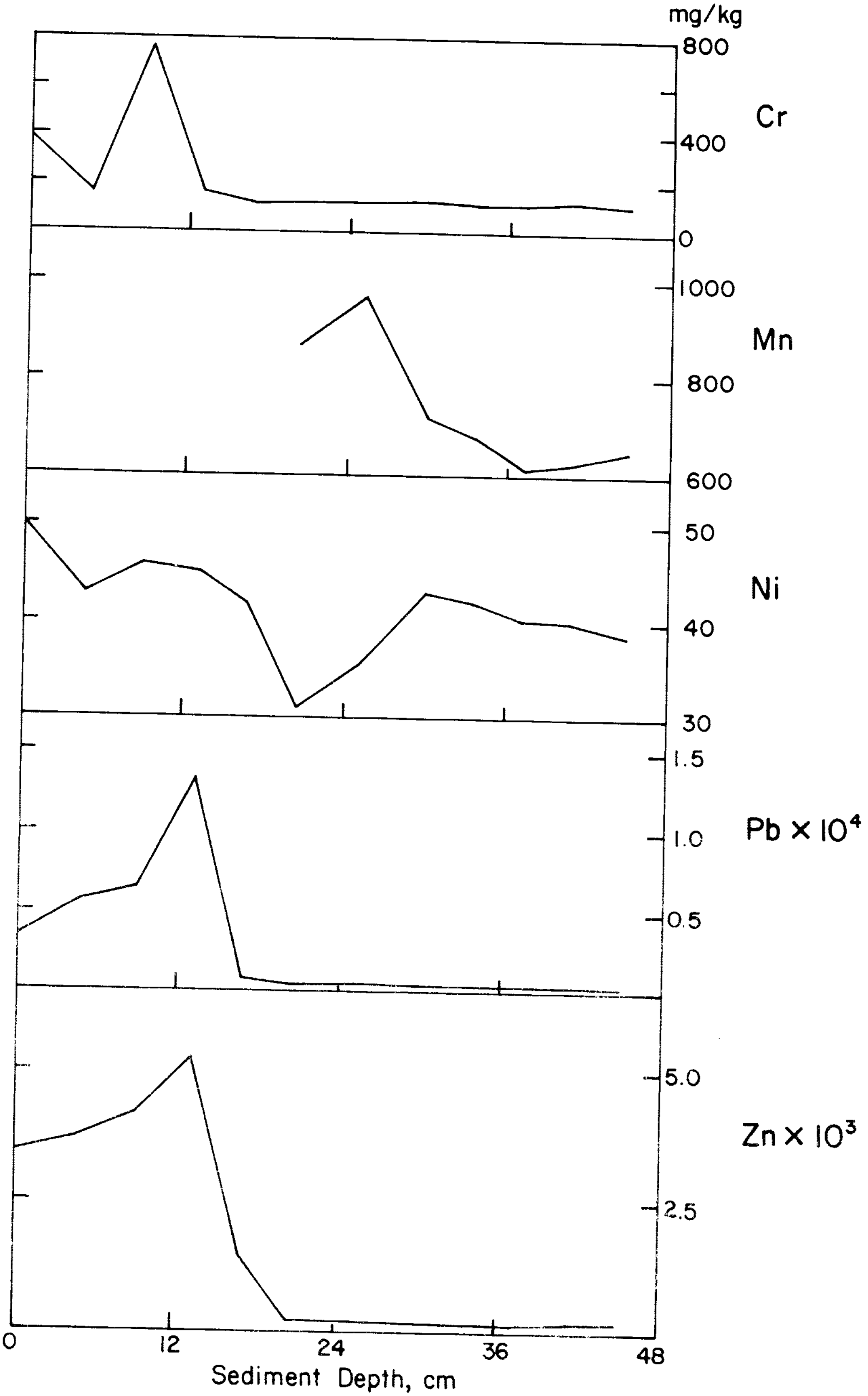

Figure 56(b). Atomic Absorption Analysis of Core H (Powderhorn Bay, 1.3 km From Tributary Creek, 8 m Water-depth).

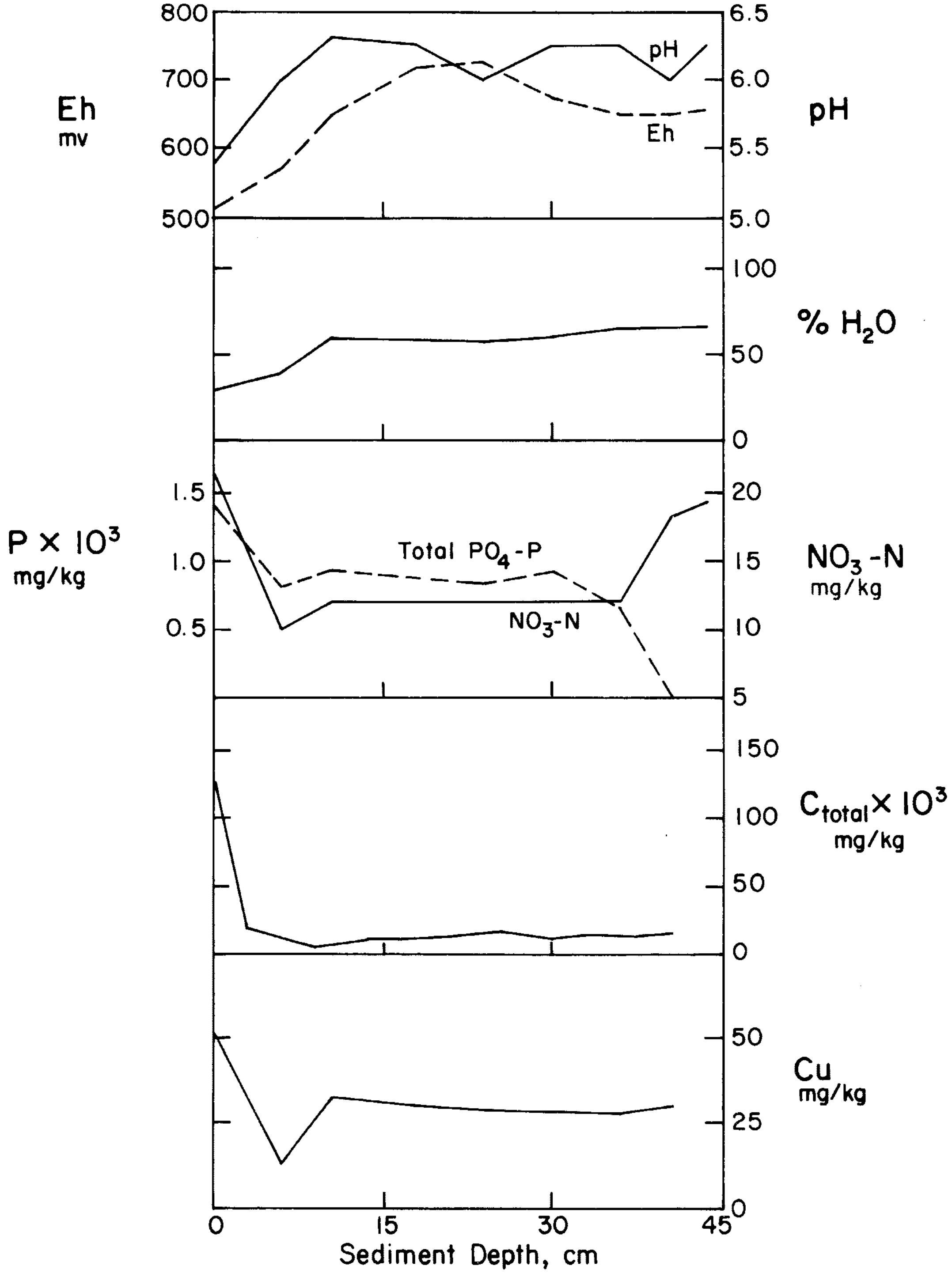

Figure 57(a). Standard Chemical, Total Carbon and Atomic Absorption Analysis of Core I (.4km from Mouth of Carlin Creek, 7m Water-depth).

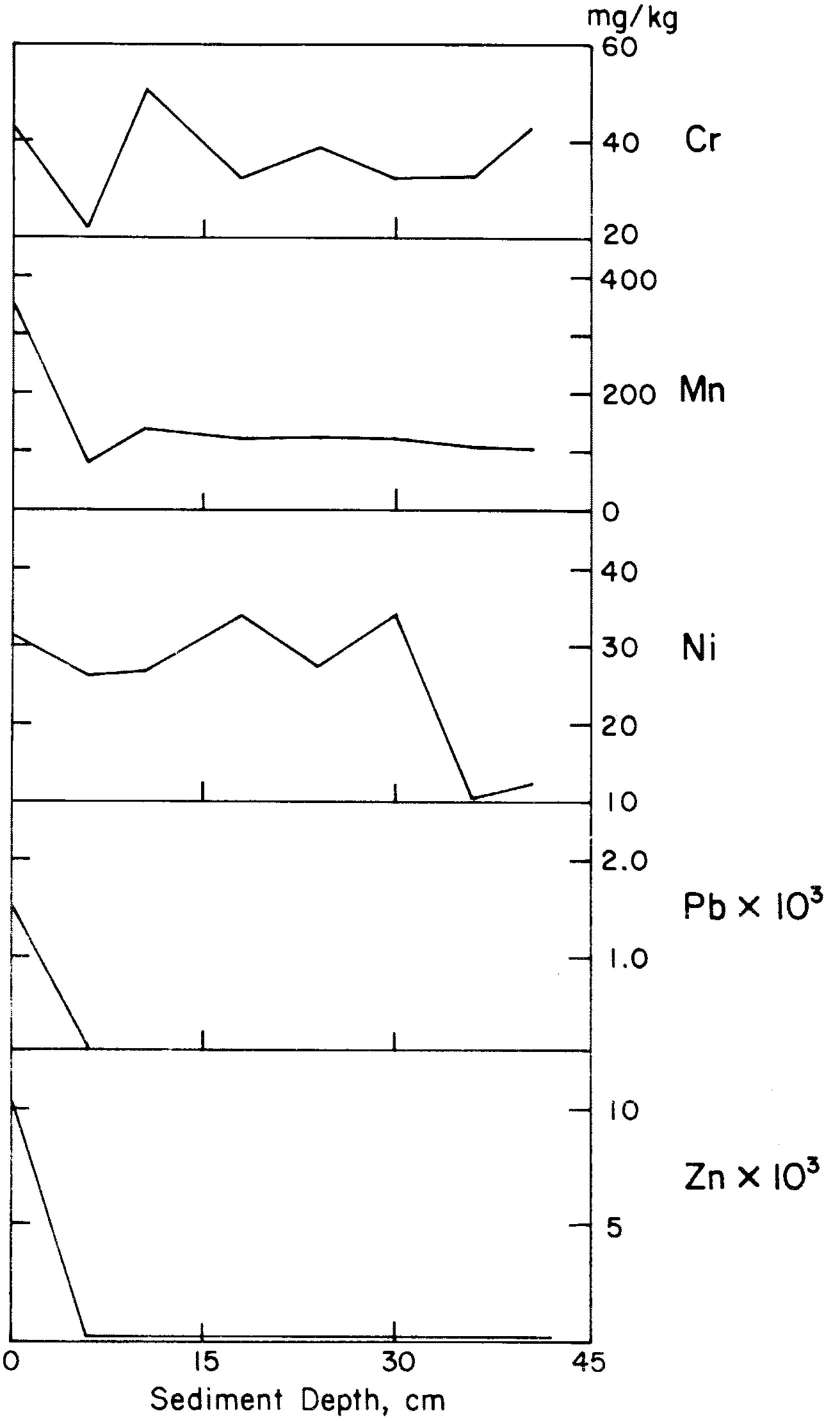

Figure 57(b). Atomic Absorption Analysis of Core I (Carlin Bay, .4 km From the Mouth of Carlin Creek, 7 m Water-depth).

Core J (24cm length)

Core J was taken in Mica Bay 1 km outward from Mica Creek in 13m of water. The composition of sediments in this area is a thick, heavy clay in which mica is embedded. The coring device could obtain only 20-cm-length cores even after repeated drops. Mica Bay is somewhat protected from lake currents but showed considerable evidence of metallic contamination above that of background (Figures 58a and 58b). The greatest influence upon this area is no doubt Mica Creek, with some input by several small creeks. Another core taken in the midbay region (3 km from Mica Creek) was analyzed by neutron activation methods. This core also showed considerable increases of metallic elements in the upper 2-5cm layers. The amounts present in the layers of the latter core are shown as mg/kg in parentheses following the elemental symbol; the mean amounts present in the lower layers to the 43cm depth are shown in brackets. Hg (5.9) [.9]; Th (11.5) [10.7]; Cr (64) [56.9]; Hf (3.0) [2.5]; Ba (608) [443].

Core K (44cm length)

Core K was driven (at the outlet of Coeur d'Alene Lake) in the Spokane River in 12m of water. This core was taken 9 months after Core 11 was driven some 2.5km to the southeast. The results are surprisingly similar. The measured values which are relatively close and the sediment layers containing the higher metallic contents of both cores are limited to the upper 5cm of sediment (Figures 59a and 59b). There is also a mixture of small wood fragments and chips in the upper 2-3cm of sediment layers as a result of log storage in the area. Trees have been cut in the Coeur d'Alene drainage area for the past 50-70 years. The logs are floated down the rivers and stored in this and other locations throughout the lake until processed into lumber, pulp and other wood products.

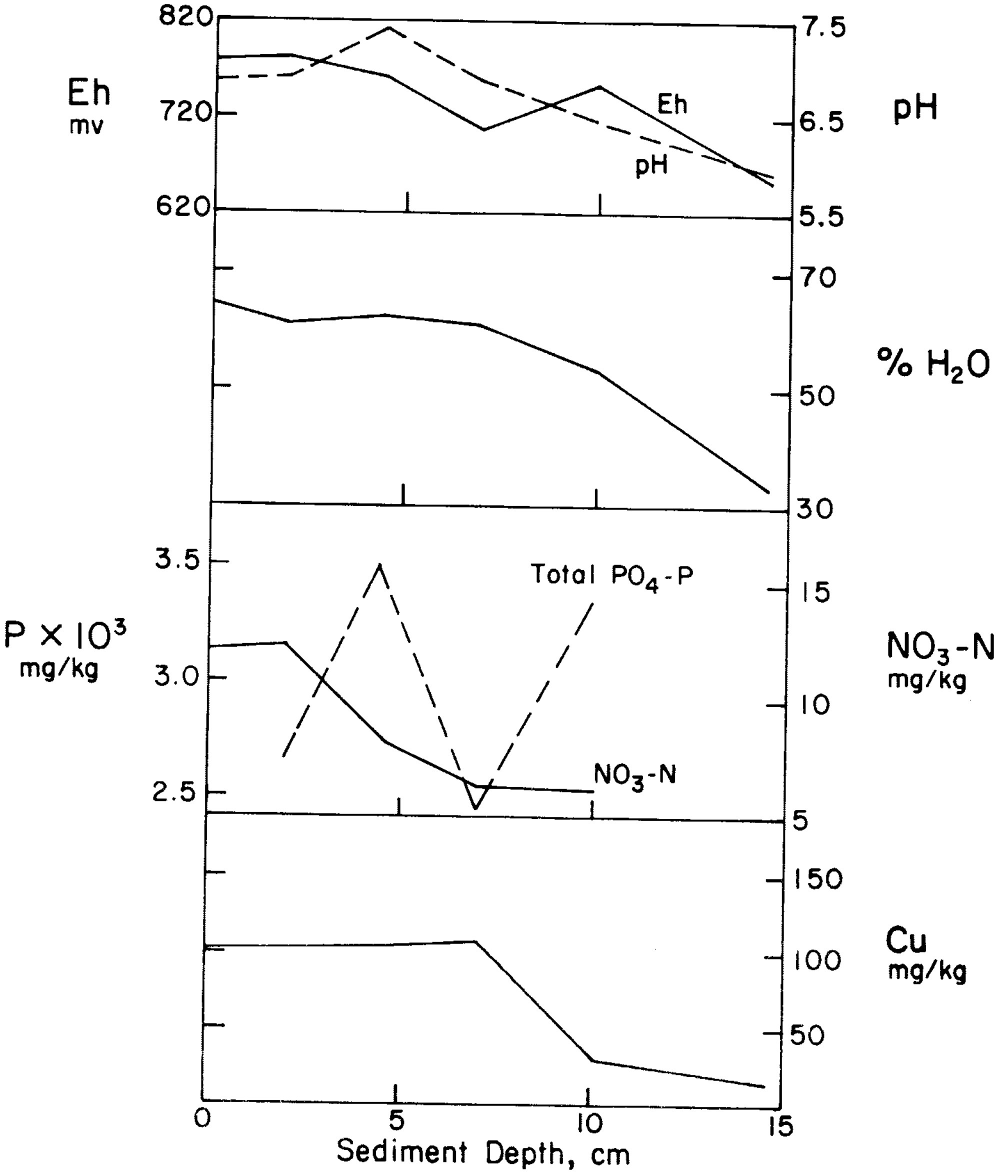

Figure 58(a). Standard Chemical and Atomic Absorption Analysis of Core J (1km out from Mouth of Mica Creek, 13m Water-depth).

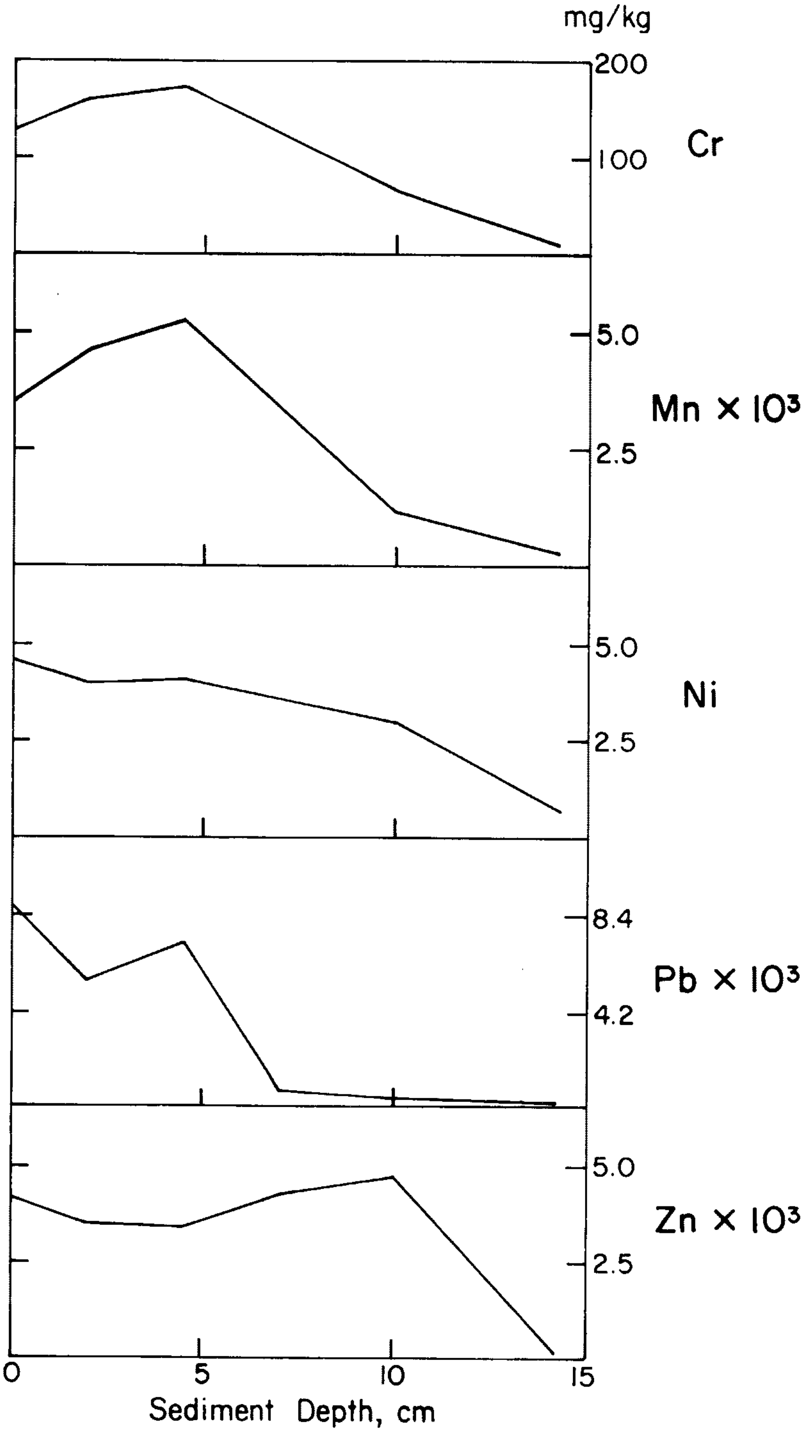

Figure 58(b). Atomic Absorption Analysis of Core J (Mica Bay, 1 km Out From Mouth of Mica Creek, 13 m Water-depth).

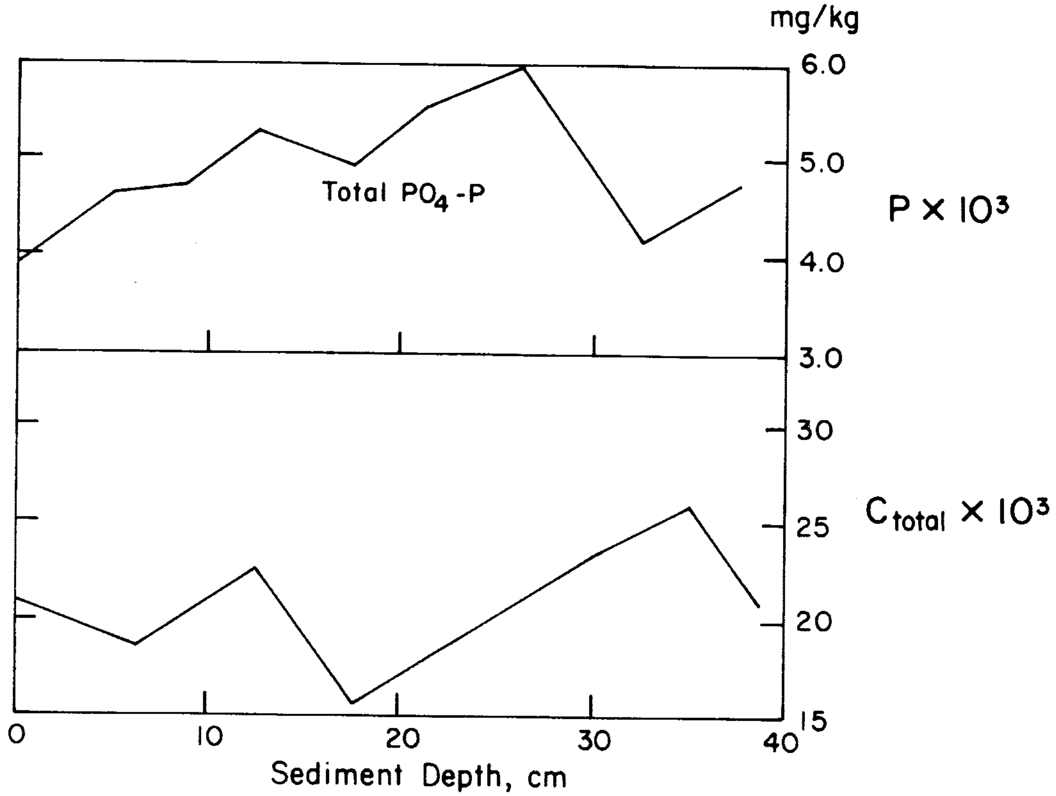

Figure 59(a). Standard Chemical, Total Carbon and Atomic Absorption Analysis of Core K (Outlet to the Spokane River, 12m Water-depth).

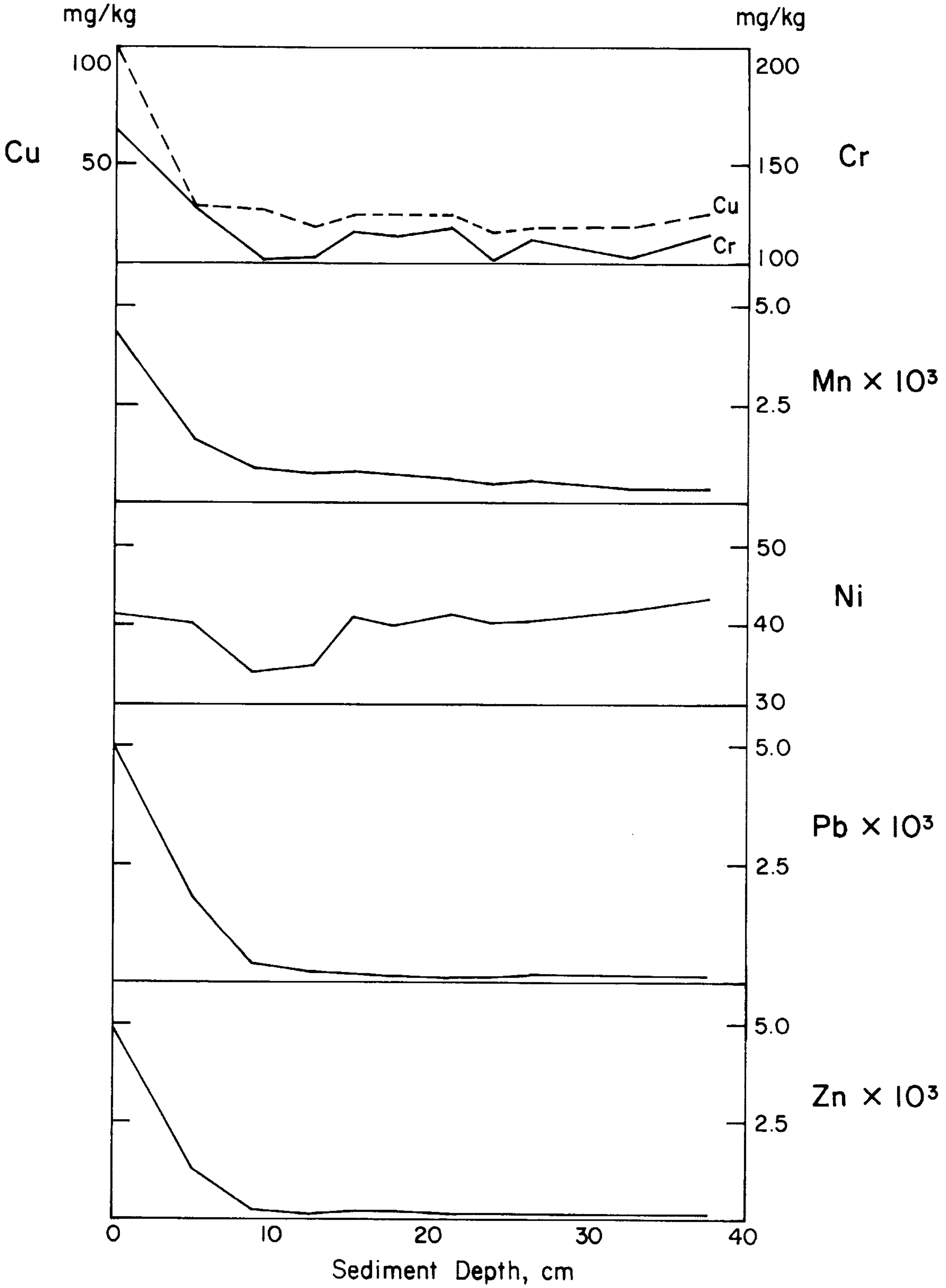

Figure 59(b). Atomic Absorption Analysis of Core K (Outlet to the Spokane River, 12 m Water-depth).

Core L (53cm length)

Core L was driven in Bennett Bay--.14km southward from U.S. I-90 in 9m of water. Throughout the entire 53cm length no definite trend in the metallic content of sediments were established for those metals tested for (Cu, Cr, Mn, Ni, Cr, Pb and Zn). Zinc and Pb initially showed higher than background levels in the upper 1.0cm. The Cr, Ni and Mn constituents were higher at lower levels (45 to 53cm). The bay is relatively sheltered from lake currents but it is surmised that winds may have aided in the distribution of Pb and Zn in the upper layers. The higher levels of Cr, Cu, and Mn that occur in the lower sediments may be the result of disturbances unrelated to mining activity (Figures 60a and 60b).

Coring Study Summary

Twenty-one cores were taken in this investigation along the lengthwise axis and in the bay areas of Coeur d'Alene Lake; 18 of the cores were analyzed subsequently for metallic content. Cores taken northward from the Coeur d'Alene River delta (6 to 11) steadily decreased in the depth of sediments containing excessive amounts of heavy metals. Cores 1 to 5 were driven and the resultant measurements made as part of our Title I study. Core 6 was retrieved approximately 2km north of the earlier transect. The layer of heavy metals in Core 6 was present from the surface or 0 layer to the 19cm depth. The metal-containing layer of each core taken thereafter northward along the N-S axis of the lake decreased by 2-4cm at each location until at the outlet of the lake the depth of sediment containing heavy metals in excess of background was only 5cm (0-5cm depth) in thickness. A similar pattern was found in the northern bay regions, depending upon how protected the bays were

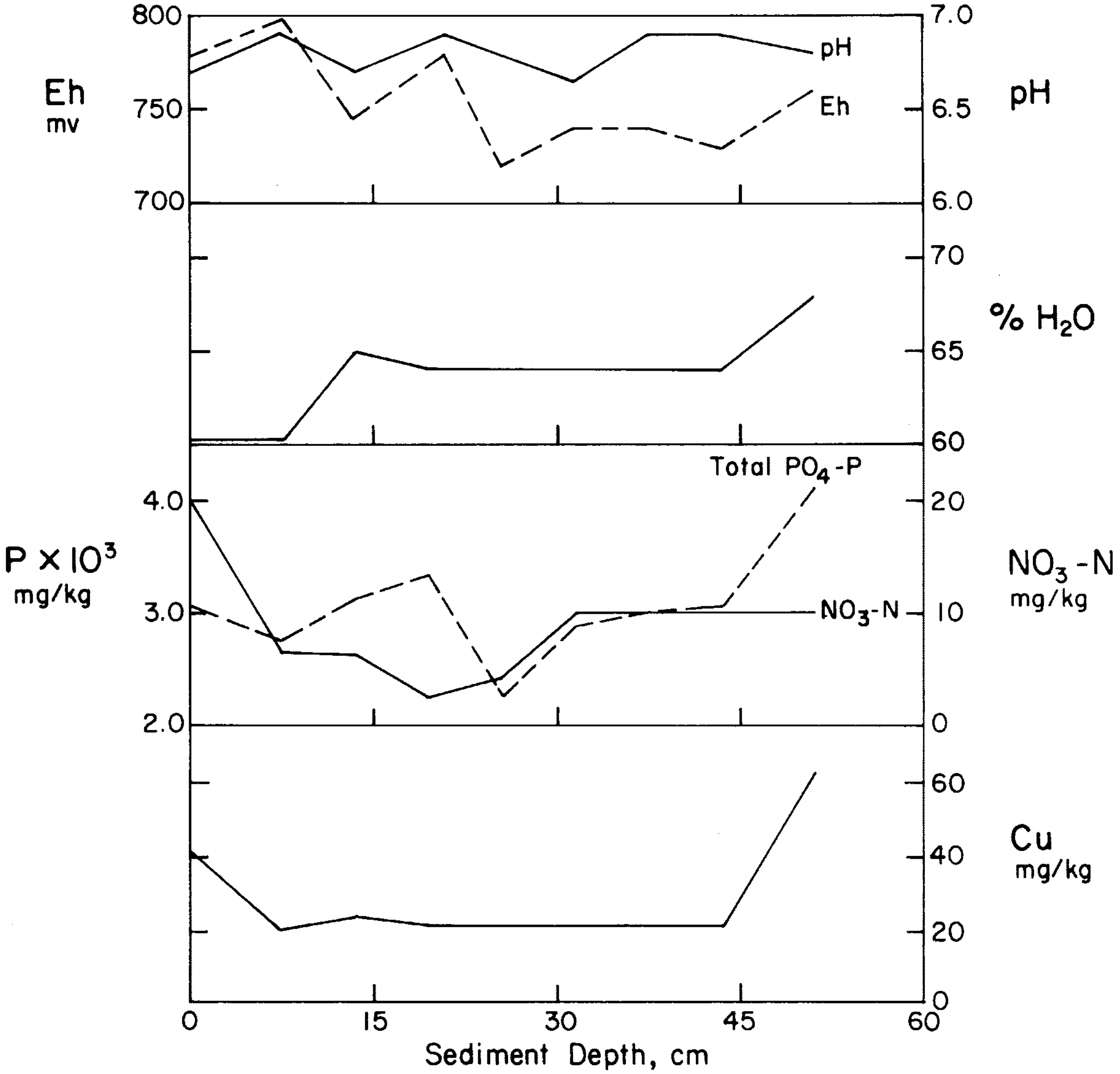

Figure 60(a). Standard Chemical and Atomic Absorption Analysis of Core L (Bennett Bay, .14km South of U.S. I-90, 9m Water-depth).

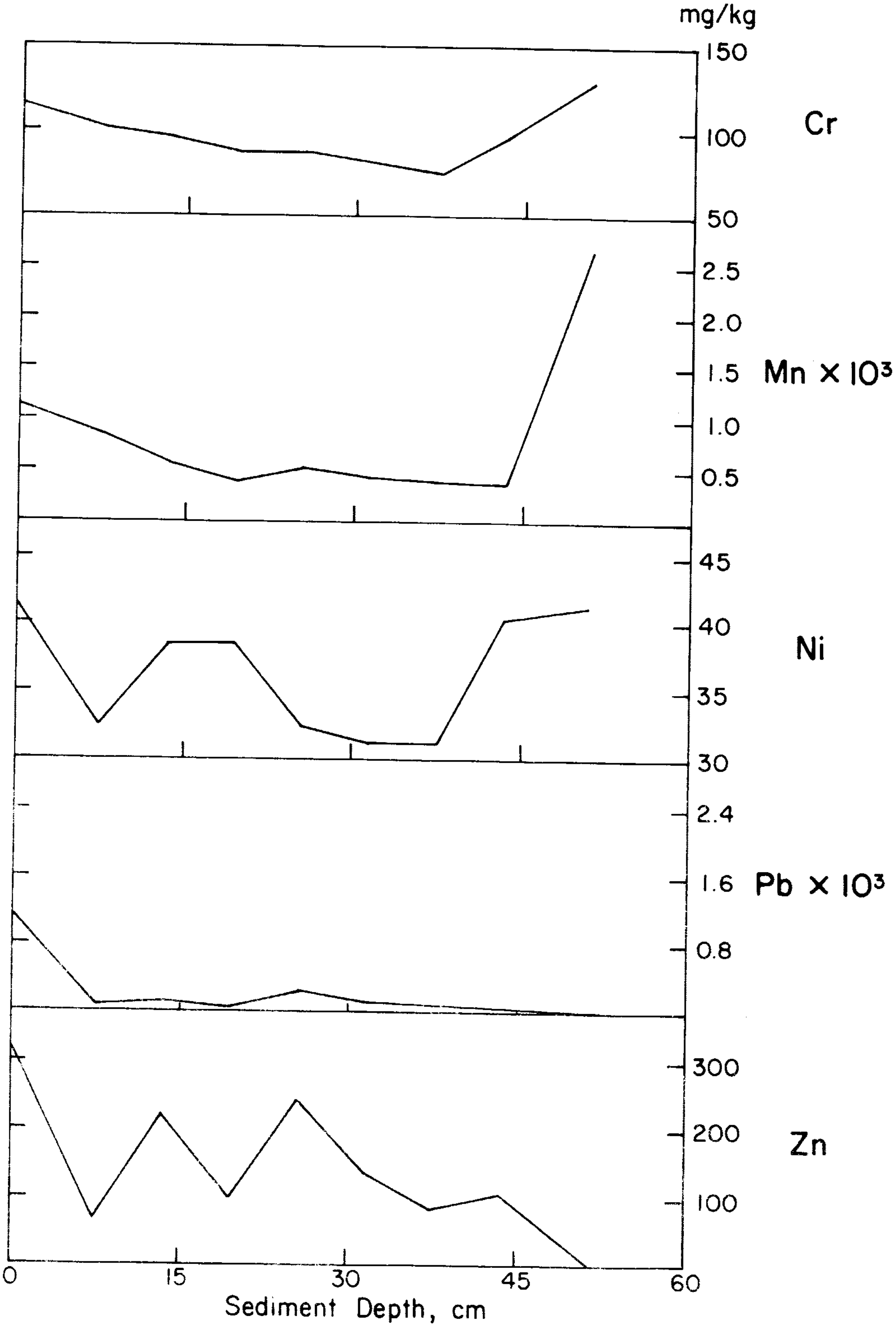

Figure 60(b). Atomic Absorption Analysis of Core L (Bennett Bay, .14 km South of U.S. Interstate 90, 9 m Water-depth).

from the flow of water and most likely--to some extent--the wind. Usually the metallic layers were 3-5 cm less in depth than cores driven outside the bays, with the exception of Core H, which shows nearly the same metallic layer depth as the main axis, Core 7. Observation in that area indicates that movement of sediments by wind-influenced currents may account for the heavier deposition. The flow of the Coeur d'Alene River as it courses through the lake also appears to pass close by the mouth of this bay, as evidenced by muds carried by the river during spring runoff.

Cores 12, 13, 14 and 15 were driven along the main axis of the lake from the southern toward the northern end. Cores 12 and 13 showed a slight increase above background, but Core 14 off Conkling Park picked up the southerly drift of metals from the Coeur d'Alene River. Zinc, for example, is 4-5 times above background and Pb is nearly twice as much at a point 6.0 km south of the delta. Wind action and lake circulation probably account for this distribution.

In the area of Core 15, surface sediments contain as much as 3500 mg/kg Zn. Cores A, B and C were driven in nearby bay areas of the southern portion of the lake and for the most part show levels of metals slightly higher than background. These higher amounts most likely are due to human activities in the areas rather than mining.

At present, the sediment layers containing the metals probably do not represent an environmental hazard but, should the lake become eutrophic with anaerobic conditions in the lower layers, the situation could change rapidly. As the metals became soluble, they could participate increasingly as constituents of the aquatic food chain and no doubt exert a selective influence upon both producers and consumers.

C. Laboratory Study of Zn Uptake by Sediments (Clays)

Zinc in Fresh Waters

Zinc is found in most natural waters. In U.S. surface waters Kopp and Kroner (1970) found concentrations of up to 1183 μg/1. In our study, Zn in the particulate state (retained on a .45μ membrane filter) was found in 64% of the samples, with a mean of 62 μg/1. For the dissolved state, the frequency was 77%, with a mean of 64 μg/1. In streams, Zn may be transported in the form of discrete mineral grains, adsorbed on inorganic and organic particulate matter, in solution as simple ionic and neutral species or as Zn complexes. In a given environment, the physicochemical state of Zn is the major determining factor in its availability to aquatic biota, and the toxicity of Zn to given species will depend upon the metabolism of the organisms.

In our earlier study of heavy metal pollution of the Coeur d'Alene Lake-Spokane River system (Funk, Rabe, Filby *et al.*, 1973), Zn was (with few exceptions) the most prominent of all so-called "trace metals." Zinc concentrations as high as 21 mg/1 were found in Coeur d'Alene River waters in the region of the mining activity (Table 27). Sediment cores from Coeur d'Alene Lake contained Zn concentrations of up to 13,000 mg/kg.

The presence of Zn in aquatic ecosystems may be due to natural causes or to human activity. Zinc may be brought into the streams and lakes by weathering of transported and/or deposited minerals. This input may be increased by poor soil conservation practices which lead to erosion, but it is usually considered that this contribution to the dissolved Zn load of bodies of water is not very important. Mining operations, including smelting and processing of ores, appear to be the major source of Zn in this area. Table 27 shows Zn values for two branches of the Coeur d'Alene River. The North Fork is a relatively unpolluted stream whose watershed is in the Coeur d'Alene National Forest. It is taken as representative of the background Zn concentration in the area. The South Fork flows through the Kellogg-Wallace mining district (Zn, Pb and Ag extraction and processing), and influence of the mining and processing effluents can be seen readily in the main stem of the Coeur d'Alene River.

Table 27. Dissolved Zinc Concentration (mg/l) in the Coeur d'Alene River, Northern Idaho, During Low Flow, 1968-1971. (Adapted from Funk, Rabe, Filby *et al*., 1973.)

Sampling Station	Year			
	1968	1969	1970	1971
North Fork	0	0.1	0.1	0.1
South Fork	15.1	21.0	17.3	19.9

Not only is Zn widely distributed throughout the aquatic environment, but it tends to remain in ecosystems indefinitely. Zinc may be removed temporarily from the water phase by aquatic biota that utilize it as a nutrient or inadvertently ingest it and, more importantly, by adsorption on suspended matter or bottom sediments. But the metal is still present in the system and it becomes available again when the organisms die and decay or when it is desorbed from the solid phase upon changes in physical and/or chemical conditions.

Zinc Uptake by Organisms

In small amounts, Zn is a beneficial nutrient required in particular for the activity of enzymes. Carbonic anhydrase (CO_2 formation and regulation of acidity), carboxpeptidase (protein digestion) and alcohol dehydrogenase (alcohol metabolism) all require Zn. Buhler (1973) defines three levels of exposure-response for essential metals such as Zn. In the first level, the organism suffers from deficiency; in the second, the supply of metal is adequate; and, in the third, physiological damage occurs.

It is generally believed that Zn is not very toxic to humans, which explains why the United States Public Health Service drinking water standard of 5 mg Zn/l is the highest allowable concentration for any of the trace metals (Manahan, 1972). However, Zn is known to affect aquatic organisms, and Malacea and Gruia (1964) recommended that this standard be lowered. Zinc is, with Cd, Cu, Pb, Hg and Ag, one of the metals most toxic to fish, and concentrations from .01 to 20 mg Zn/l have been reported as toxic, depending upon the species and the water conditions (Buhler, 1973).

Zinc is toxic to many fresh water organisms. The metal concentrates in some plants and animals, but generally decreases further up the food chain. In our Title I study of the Spokane River (Funk, Rabe, Filby _et al._, L973), algae and detritus consumers such as the larva of the caddis fly, _Hydropsyche sp._, and the nymphs of the mayfly, (_Baetis sp._ , were found to concentrate Zn and other metals. High Zn concentrations also were found in the snail _Physa sp._, which feeds on algae and detritus. In the same study, mean Zn concentrations of 80, 119 and 200 mg/kg were found in the filter organs (kidney and liver tissues) of the perch (Perca flavescens), the black bullhead (Ictalurus melas) and the squawfish (Ptychocheilus oregonensis), respectively.

With the stickleback (Gasterosteus aculeatus L.), acute poisoning occurs with only .7 mg Zn/1, and there is some evidence that coagulated mucus is formed on the gill membranes and that the impaired respiration of the fish leads to asphixia (Jones, 1939). However, Lloyd (1960), using ^{65}Zn as a tracer, suggested that death was due not to coagulation of mucus but to damage of gill tissues.

Sublethal concentrations of Zn also adversely affect aquatic species. Zn is found to retard growth, to delay sexual maturity and to increase the mortality of fry of the common guppy (Legistes reticulatus) (Crandall and Goodnight, 1962). Podubsky and Stedronsky (1951) reported that Zn killed fish eggs before hatching time. Also, the spawning migration of the Atlantic salmon is affected by Zn pollution (Saunders and Sprague, 1967). Reports of the disturbance of reproduction and development of animals by Zn are not limited to fish. The susceptibility of daphnids to Zn has been shown to increase during moulting (Anderson, 1948) and, since many zooplankters moult several times during their growth, the total effect may be of importance.

The presence of Zn is not necessarily detrimental to all species of an ecosystem. Some fungi and slime-forming bacteria can grow well in high Zn concentrations, which is apparently due to the release of nutrients from decaying periphyton (Williams and Mount, 1965).

Zinc adsorbed on suspended matter and bottom sediments generally is thought to be less toxic because it is less available to aquatic biota, but filter-feeding organisms can accumulate large amounts of Zn. Mount (1966) explains the toxicity of suspended Zn by assuming that it is partially dissolved in the neighborhood of the gills because in that region the pH is lower than in the surrounding water due to CO_2 excretion. The chemical state of Zn also seems to be of some importance. Salmonid fish were found to tolerate supposedly lethal Zn concentrations in Norway (Grande, 1966), and a similar effect was found in the Coeur d'Alene River drainage system (Funk, Rabe, Filby et al., 1973). It seems likely that complexation, probably with organic matter, has a masking effect that reduces toxicity. Another possible factor that might contribute to this phenomenon is increased tolerance after adaptation (Goodman, 1951).

Because of the masking effect mentioned above, toxic conditions leading to death are probably rare and, even then are localized in areas of heavy pollution (e.g., Coeur d'Alene River at Kellogg, Idaho). However, the effects of Zn poisoning on growth and reproduction of many species are very significant. This condition can lead to slow extinction of those species that are the most sensitive to the presence of Zn.

Availability of Zinc

The importance of Zn in fresh-water ecosystems is related to its geochemical characteristics. Zinc is one of the most common trace elements in the earth's crust, and its average concentration in the lithosphere is 65 mg/kg. As discrete minerals it occurs mainly as sphalerite (ZnS) and to a lesser extent as smithsonite ($ZnCO_3$) and willemite [$Zn_2(SiO_4)$]. In aluminosilicate minerals, Zn^{2+} can substitute for Mg^{2+}, Fe^{2+} and Al^{3+}.

Zinc does not display a multiple valence, and thus Zn chemistry is the chemistry of the +2 state. It is not a transition metal, but there is some tendency to form complexes of the transition-metal type.

Solubility products from Bjerrum *et al*. (1958) are given in Table 28 for several of the more common soluble Zn species found in natural waters. Zinc can occur at fairly high concentrations in streams and lakes in the soluble state except in areas containing sulfide ions. Hydroxides, carbonates and phosphates of Zn do not precipitate under normal conditions because a fraction of soluble Zn may be complexed and therefore is masked to precipitation.

Table 28. Solubility Products of Some Selected Zinc Salts. (Adapted from Bjerrum *et al*., 1958.)

Salt	Solubility Product
ZnS (a,sphalerite)	$10^{-23.8}$
$Zn(OH)_2$	$10^{-16.6}$
$ZnCO_3$	$10^{-10.7}$
$Zn(PO_{4\ 2/3})$	$10^{-10.7}$

Organically bound Zn has been shown not to be in chemical equilibrium with the inorganic forms of Zn (Duursma, 1972). Because of the previous considerations, Zn is one of the most geochemically mobile of the heavy metals.

All Zn minerals are too soluble to be effective controls for the small Zn concentrations found in most bodies of water. It is more probable that these low amounts of Zn are due to adsorption on clay minerals and organic matter or to insufficient supply.

In fresh water, soluble Zn can occur in different chemical forms (ion, organic and inorganic complexes). The divalent cation Zn^{2+} is the predominant ionic species, $Zn(OH)^+$ not being present in significant amounts because the hydrolysis constant has a value of $10^{-9.6}$. Nelson et al. (1966) found that 83 to 100% of the Zn in the waters of the Columbia River, Washington was in cationic form. In the Coeur d'Alene River, Zn was found to occur from 51 to 98% in cationic form, from 1 to 5% in anionic form and from 2 to 44% in neutral form (Seamster and Filby, 1974). On the other hand, Hodgson et al. (1960) showed that on the average 60% of the Zn in solution in natural waters is in complexed form. However, we still know very little about the details of the physical and chemical forms of Zn in natural waters. Gross analysis values are not very meaningful and they are being replaced increasingly in the literature by figures in suspended and dissolved concentrations. Nevertheless, we need to improve our understanding of the mechanisms controlling the distribution of Zn between the solid and aqueous phases. A study of Coeur d'Alene river waters showed that 83 to 94% of the total Zn was in the dissolved state (Seamster and Filby, 1974).

Several workers (Randhawa, 1965; Schnitzer and Skinner, 1966; and Hodgson, 1963) have suggested that humic and fulvic acid fractions of organic matter play an important role in the retention of Zn by soils. The uptake of Zn by humic materials involves both cation exchange and complexation (Rashid, 1971). Himes and Barber (1957) presented evidence for carboxylic and phenolic group bonding of Zn with organic matter. Humic materials originate from chemical and biological degradation of plants and therefore are distributed widely throughout the environment, including aquatic ecosystems.

Clay minerals make up a large fraction of the suspended load of streams and of the bottom sediments of rivers and lakes. Their importance is accentuated by their large surface area per unit weight. Because of their adsorbing capacity, the clays in the solid load of natural waters act as decontaminating and transporting agents and as buffering reservoirs for dissolved cations which are present in the system. Judson and Ritter (1964) found that for U.S. waters the weighted average concentration of suspended matter was 602 mg/1, the Colorado River itself carrying up to 13,930 mg/1. It is certain that clay minerals are not the only contributors to this load, but for the reason given above they are an important factor together with humic materials and metal oxides (e.g., $Fe_2O_3 \cdot nH_2O$, $MnO_2 \cdot nH_2O$).

The clay minerals and organic matter of soils are the main vehicles for retention of nutrients where they will be available to plants. Thus, before the recent concern with heavy metal pollution, most of the work done on the adsorption of Zn was published in the soils literature. Also, the presence of radionuclides from bomb testing and nuclear power stations in many aquatic systems has generated additional interest in the study of the removal of trace elements from solutions.

Zinc is thought to be held by sedimentary minerals partly adsorbed on the surface of colloidal particles and partly inside the clay mineral lattices themselves, probably substituting in normal Mg^{2+} sites (Elgabaly, 1950; White, 1957). Elgabaly also concluded that nonextractable Zn had entered the octahedral layer of the clay lattice, where it was fixed in holes not occupied by Al atoms. But subsequent work has shown that most of this nonextractable Zn actually can be removed with acid.

Udo _et al_. (1970) found Langmuir adsorption isotherms for calcareous soils. Chester (1965) found the adsorption of Zn in sea water to reach saturation for a concentration of approximately 200 μg/1. Bingham _et al_. (1965) showed that the anion of the Zn salt used in adsorption experiments was of limited importance. In the case of the acetate, Zn uptake was found to exceed the cation-exchange capacity (CEC). Acetate retention appeared to be independent of Zn retention, thus ruling out the adsorption of zinc as CH_3COOZn^+.

If the uptake of Zn by clay minerals were due to an ion-exchange mechanism, one should be able to describe the reaction by a mass-action relationship of, for example, the Kerr type,

$$\text{Ca-X} + \text{Zn}^{2+} \rightleftharpoons \text{Zn-X} + \text{Ca}^{2+},$$

with an equilibrium constant

$$k + \frac{[\text{Zn-X}]_{\text{clay}}\ [\text{Ca}^{2+}]\ \text{solution}}{[\text{Ca-X}]_{\text{clay}}\ [\text{Zn}^{2+}]\ \text{solution}},$$

where X represents the clay. However, the activities of the four terms involved in the value of the equilibrium constant are difficult to determine, and thus k is usually not constant. The inconsistencies of simple mass-action expressions are thought to be due to the combined effect of the nonhomogeneity of the exchange medium and of the mixed character (not purely ionic) of the adsorption (Kown and Ewing, 1969).

De Mumbrum and Jackson (1956) showed that montmorillonite can adsorb Zn beyond its cation-exchange capacity, especially for alkaline pH values. They explained this phenomenon by either or both of the following mechanisms: adsorption of the hydrolyzed form $ZnOH^+$ and/or precipitation of the hydroxide $Zn(OH)_2$.

In summary, Zn appears to be removed by clay minerals from the bulk of the solution in two steps. The first mechanism probably is due to electrostatic forces, and it seems reasonable to assume that the slower step involves diffusion into specific exchange sites. The complexity of the situation occurring at the water-clay interface prevents an ion-exchange mechanism to be expressed simply by a mass-action expression. As long as Zn acetate is not used, the anion influence is not significant.

Objectives of Laboratory Study

Our objective in this investigation was a better understanding of the role of clays in the geochemistry of Zn^{2+} in fresh waters. (For an expanded discussion of methods and procedures, see Bourg, 1974.) The distribution of this cation between clay minerals and the aqueous phase in natural waters is part of the key to the regulation of the concentration of dissolved Zn and therefore of its transport in streams, rivers and lakes.

As previously stated, clay minerals, iron and manganese oxides and organic suspended matter (including humic materials) are the main agents responsible for the uptake of metals in natural waters. The interaction of metal ions with particulate organic matter in streams is not very well characterized at the present time. The adsorption of metal cations by oxides in water also has been documented partially (Posselt et al., 1968). However, in this work we have considered the adsorption of Zn^{2+} (as zinc sulfate) by three common clay minerals in a fresh-water medium. Some caution therefore is advised in the extrapolation of the conclusions to real aquatic environments.

Zinc sulfate was selected as the Zn salt for two reasons. Zinc chloride is very hygroscopic and therefore is difficult to weigh accurately. Zinc sulfate ($ZnSO_4 \cdot 7H_2O$) was preferred to the nitrate because in natural waters sulfate ions are found almost always in higher concentrations than are nitrate ions.

The Zn introduced into an aqueous solution affects its pH because of the hydrolysis reaction: $Zn^{2+} + H_2O \rightleftarrows Zn(OH)^+ + H^+$. For near neutral solutions, the pH decreases approximately by one-half unit when the Zn concentration is multiplied by .10. Soil solutions are buffered strongly because of their high clay content, and pH change during adsorption of Zn is small. At concentrations of particulate matter found in streams, lakes and oceans, there is an appreciable change of pH upon introduction of Zn^{2+} ions if the system is not buffered. Because the adsorption of Zn on clays is pH-dependent, it is necessary to buffer the solution. In the study of uptake of Zn under marine conditions, Chester (1965) used Na_2CO_3 and $NaHCO_3$ to buffer seawater samples at pH 8.0. However, the choice of a buffering system in the pH range of fresh waters is restricted by the need to avoid precipitation of zinc salts (e.g., phosphates), to avoid complex formation [e.g., $Zn(NH_3)_4 2+$] and to avoid strong adsorption of the buffering agent on the clay. The approach taken in this study was to use 2-amino-2-(hydroxymethyl)-1,3-propanediol, more commonly known as tris(hydroxymethyl)aminomethane, or TRIS, to buffer the solution. The presence of this amine must be kept in mind during the interpretation of the results.

The input of Zn into natural waters is usually not large enough to change the ionic strength of the medium, especially in hard waters. Therefore, cesium perchlorate (.010 M) was added to the TRIS to keep the ionic strength constant. This salt usually is chosen for that purpose because neither Cs^+ nor $C10_4^-$ is involved in complexation reactions.

Natural waters have a broad pH range; extremes of 1.7 for an African lake and of 12.0 for some Japanese lakes have been reported in the literature. However, most of the surface waters have pH values in the range 6.0 to 8.0. For bottom sediments, pH values as low as 5.0 are common (Funk, Rabe, Filby et al., 1973; Williams et al., 1970). This study therefore is restricted to the pH range 5.0 to 8.0.

Clay minerals in fluvial sediments usually reflect the composition of the rocks and soils from which they are derived. Kennedy (1965), in a survey of stream clays of the U.S., showed that the most prevalent clay minerals were montmorillonite, illite and sometimes kaolinite, depending upon the geographical location of the streams. Holmes and Hearn (1942) analyzed the alluvial material deposited by the Mississippi River, and they found 5-15% kaolinite, 25-45% montmorillonite and 40-60% illite. Illitic minerals are predominant in the bottom sediments of the Coeur d'Alene Lake (Dunigan, 1972). The order of abundance of minerals in deep-sea sediments (illite, montmorillonite, and to a lesser extent kaolinite and chlorite) also should be indicative of the suspended load of rivers and streams. In addition to their ubiquity in sediments, illite, montmorillonite and kaolinite were chosen because of their different structural characteristics.

In order to have a simple system, the clays were saturated with a single cation. To stay as close as possible to natural conditions, two ways of choosing the saturating cation were available. (1) Of the cations commonly found in the dissolved state in fresh waters, Ca usually has the highest concentration (Livingstone, 1963; Sugawara, 1968). The greater the contribution of a cation to the total dissolved salt content of natural waters, the more likely this cation is to be adsorbed predominantly by the clay. If one keeps in mind that the major cations of aquatic systems do not all have the same charge, one can still assume that Ca is more involved in ion-exchange reaction with clays than Mg, Na and K. (2) One can analyze for the major exchangeable cations in the clay samples used in this study to determine which one is actually predominant. Table 29 shows that Ca is the predominant exchangeable cation for the illite and kaolinite and is second to Na for the montmorillonite used in this study.

Table 29. Major Exchangeable Cations.

Sample	Extractable Cations (meq/100 g) Direct Determination		Extractable Cations (meq/100 g) By Difference and Ratio	
	Na	K	Ca	Mg
Montmorillonite	28.20	2.45	14.50	2.24
Illite	1.53	1.89	5.06	3.96
Kaolinite	0.39	0.08	4.92	0.22

For these reasons, Ca was chosen to saturate the clays.

The influence of several factors (clay mineral type, pH, time, temperature, zinc concentration, clay concentration, ionic strength, nature and concentration of other cations) on the Zn^{2+} uptake by the three clays is discussed later. Figure 62, for example, represents the adsorption of Zn with respect to time for the three clay samples, all other factors being identical. For each clay, Zn^{2+} was adsorbed rapidly during the first 15 minutes and then at a much reduced rate. In this work, Zn^{2+} was allowed to react with the clay samples for one hour and thus describes only the most important step--the rapid one.

This system does not take into account any biologically mediated reaction. The microorganisms present in an aquatic environment certainly affect the system. In particular, the suspended matter-water interface is a favorable site for microorganisms because as they are transported they are in contact with more nutrients. The same thing happens with the attached benthic flora and fauna which, being fixed on the bottom of a stream, are exposed to constantly renewed water.

Except for the limitations mentioned above, this simple system is quite close to natural conditions. Cesium ions play the role of other cations, of which one will have a greater influence than the others. TRIS plays the role of a prevalent organic component. An important factor of natural systems is the suspended organic matter, but the behavior of Zn in the presence of humic materials as a study in itself was out of the scope of this work.

Results of Laboratory Study

The fact that the cation-exchange capacity (CEC) of clays usually increases with pH (Pratt, 1961; and Chichester _et al_., 1970) prompted a study of its effect on the Zn^{2+} uptake. TRIS solutions of various compositions (i.e., of various pH) were prepared and poured into centrifuge tubes containing 100 mg of clay sample. Zinc sulfate then was added to the medium. Figure 61 shows a strong dependence between the Zn^{2+} uptake and the pH of the solution. For illite and kaolinite this dependence becomes nonexistent at low pH. Table 30 gives the differences between the Zn uptake at pH 8.0 and 6.3.

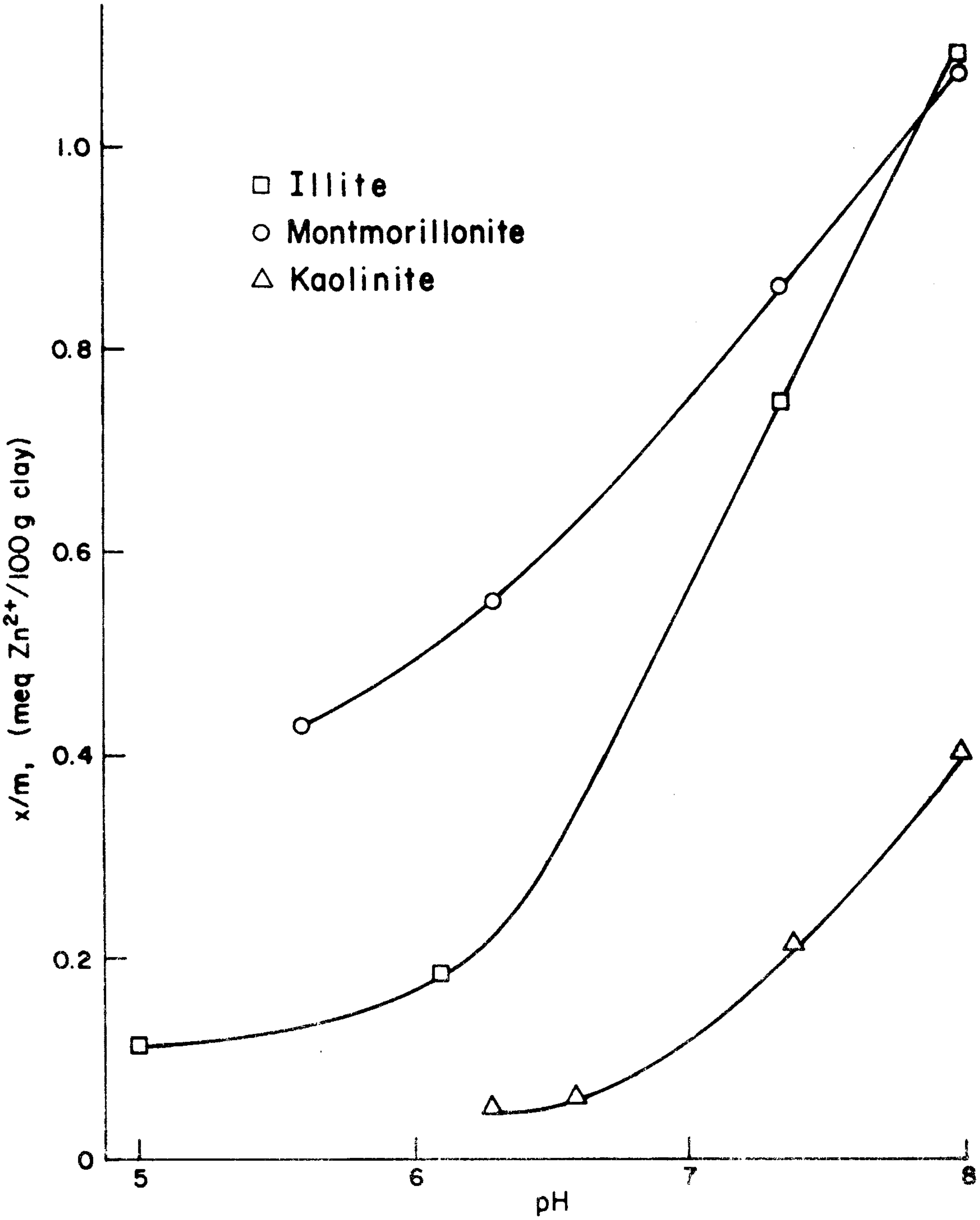

Figure 61. Uptake of Zn^{2+} as a Function of pH

Table 30. Uptake of Zn^{2+} as a Function of pH.

	Clay Sample		
	Illite	Montmorillonite	Kaolinite
Difference between Zn^{2+} uptake at pH 8.0 and 6.3 (in meq Zn^{2+}/100 g clay)	0.86	0.53	0.35

By comparing the experimental pH values with and without the presence of clay, the buffering capacities of the minerals studied were found to be in the following order: kaolinite, montmorillonite and illite. This result could be expected after looking at Table 30 because the buffering capacity of clay minerals depends upon pH-dependent exchange capacity, which in this case is followed by observing the pH-dependent Zn^{2+} uptake.

Let us now consider the possible explanations for the effect of pH upon removal of Zn^{2+} from the bulk of the solution. According to the literature (Bjerrum _et al_., 1958; Garrels and Christ, 1965; Ligane, 1966), the solubility product of $Zn(OH)_2$ has a value of $10^{-16.35}$ to $10^{-16.63}$ (Table 31). If one takes the smallest solubility product value, precipitation of the hydroxide should start to occur only at pH 7.9 for the Zn^{2+} concentration used in this experiment (3.8×10^{-5} _M_ Zn^{2+} or 2.5 mg Zn^{2+}/l). However, precipitation usually does not occur before the pH is about one unit higher than the theoretically predicted value. This supersaturation is due to the fact that the solubility of crystals decreases with increasing size. If there was precipitation, the slopes of the curves in Figure 61 should increase suddenly at about pH 7.9. And if one considers that the hydrolysis constant (Table 31) of Zn^{2+} has a value of about $10^{-9.6}$ (Bjerrum _et al_., 1958; Garrels and Christ, 1965;

Feitknecht and Haberli, 1950) at pH 8.0 there is only approximately 2.5% of the zinc in the $Zn(OH)^+$ form, unless the pH at the clay-water interface is higher than that of the bulk of the solution. This is unlikely, and several workers (Bailey et al., 1968; Harter and Ahbichs, 1967; Harter and Ahbichs, 1969) have shown evidence for the fact that the pH at the surface of clays is 2 to 4 pH units lower than that of the ambient solution, the magnitude of the difference depending upon the characteristics of the system of interest (e.g., clay mineral and ionic strength).

Table 31. Hydrolysis Constant (K_h) of Zn^{2+} and Solubility Product (K_{so}) of $Zn(OH)_2$

Log_{10} K_h	Source	Log_{10} K_{sp}	Source
-9.6	(1)	-16.35	(1)
-9.61	(2)	-16.60	(3)
-9.7	(3)	-16.63	(4)

$$K_h = \frac{Zn(OH^+)\ (H^+)}{(Zn^{2+})} \qquad K_{sp} = (Zn^{2+})\ (OH^-)^2$$

(1) Calculated from R. M. Garrels and C. L. Christ, Solutions, Minerals and Equilibria, Harper and Row, New York, N.Y., 1965.

(2) J. L. Lingane, Analytical Chemistry of Selected Metallic Elements, Reinhold Publishing Co., New York, N.Y., 1966.

(3) J. Bjerrum, G. Schwarzenbach, and L. G. Sillen, Chem. Soc. (London) Spec. Publ., No. 7 (1958).

(4) W. Feitknecht and E. Haberli, Helv. Chim Acta, 33, 922 (1950).

Since hydrolysis or precipitation of Zn^{2+} cannot explain the variation of Zn^{2+} uptake with pH, the properties of the clays themselves have to be considered. Aluminum and iron hydroxides have a net positive charge and they are adsorbed as polymers on the clay surface, where they are replaced only with difficulty. They thus lower the permanent charge of the clay by neutralizing part of it at any given pH. As the pH is raised, more of the positive charge on these polymers is neutralized by OH^-, so the effective CEC of the clay-hydroxide complex is increased. This is the main source of pH-dependent charge in the clays. Kaolinite often has a high proportion of pH-dependent charge because it was formed in an acid environment and thus has a lot of adsorbed hydroxides (McNeal, 1974). Also, broken bonds (perpendicular to layer planes) are common at the edges of clays (Al-O-Al-O in octahedral layers and Si-O-Si-O in tetrahedral layers), and silicon and aluminum atoms on these edges are hydrolyzed. Thus the charge density of the surface depends upon the pH of the solution. At low pH the permanent negative charge of the clays is due to isomorphous replacements within the crystal lattice which are not neutralized by Al or Fe oxides. These replacements are permanent and they are not affected by changes in pH. The non-pH-dependent Zn^{2+} uptake of kaolinite and illite was found to be .5 and 1.1 meq Zn^{2+}/100 g of clay, respectively.

From CEC alone, one would expect the pH-dependent charge of illite to be between that of montmorillonite and that of kaolinite. This anomaly in illite behavior may be due to a history of very low pH which would have resulted in the presence of a lot of aluminum and iron hydroxides and hence of a large pH-dependent CEC. It also could be due to a history of high pH for the montmorillonite.

Rate of the Reaction of Zn^{2+} Uptake and Effect of Temperature

The rates of the Zn^{2+} uptake reaction of the three clay samples were very similar even though the magnitudes of the uptake were different (see Figure 62). In all cases there was first a rapid removal of Zn^{2+}

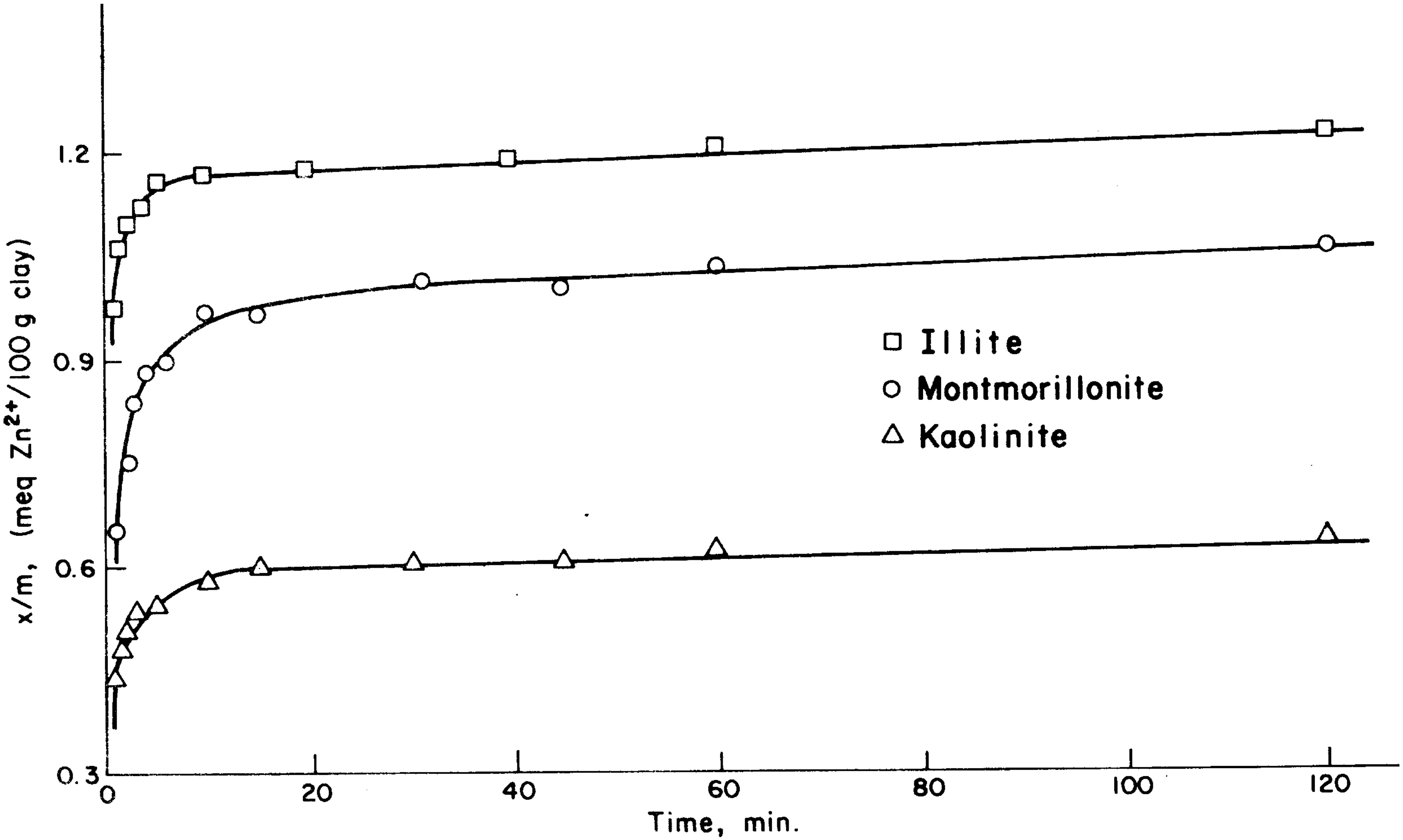

Figure 62. Uptake of Zn^{2+} as a Function of Time

from the bulk of the solution, and after 15 to 20 minutes a second step occurred at a much slower rate. These results are very similar to those of Brown (1950).

Before we go any further, we should mention that the Zn^{2+} uptake occurred in the decreasing order: illite, montmorillonite and kaolinite, whereas for the CEC it was montmorillonite, illite and kaolinite. Table 32 shows the ratio of the amount of Zn^{2+} adsorbed to the CEC for each clay. It can be seen that for illite and kaolinite the values are approximately equal, but in the case of montmorillonite the ratio is about five times smaller. There are at least three possible causes for this anomaly and they all might contribute to the observed deviation. The behavior of TRIS and that of Cs^+ might be different with montmorillonite than with the two other clays. A third possibility would be that Zn^{2+} adsorption occurs at privileged sites in kaolinite and illite as opposed to montmorillonite.

Table 32. Ratio of Amount of Adsorbed Zn^{2+} to CEC.

	Illite	Montmorillonite	Kaolinite
x/m (meq Zn^{2+}/100 g of clay)	1.20	1.03	0.61
$\frac{x/m}{CEC}$	0.097	0.022	0.109

The Zn^{2+} uptake reaction was carried out at three temperatures (15, 25 and 37 C), and for each clay sample the amount of Zn^{2+} adsorbed was found to increase with temperature (Figures 63, 64 and 65). Kinetic calculations were performed for all of these curves, but because of the nature of their shapes (large slope followed by small slope) no conclusive

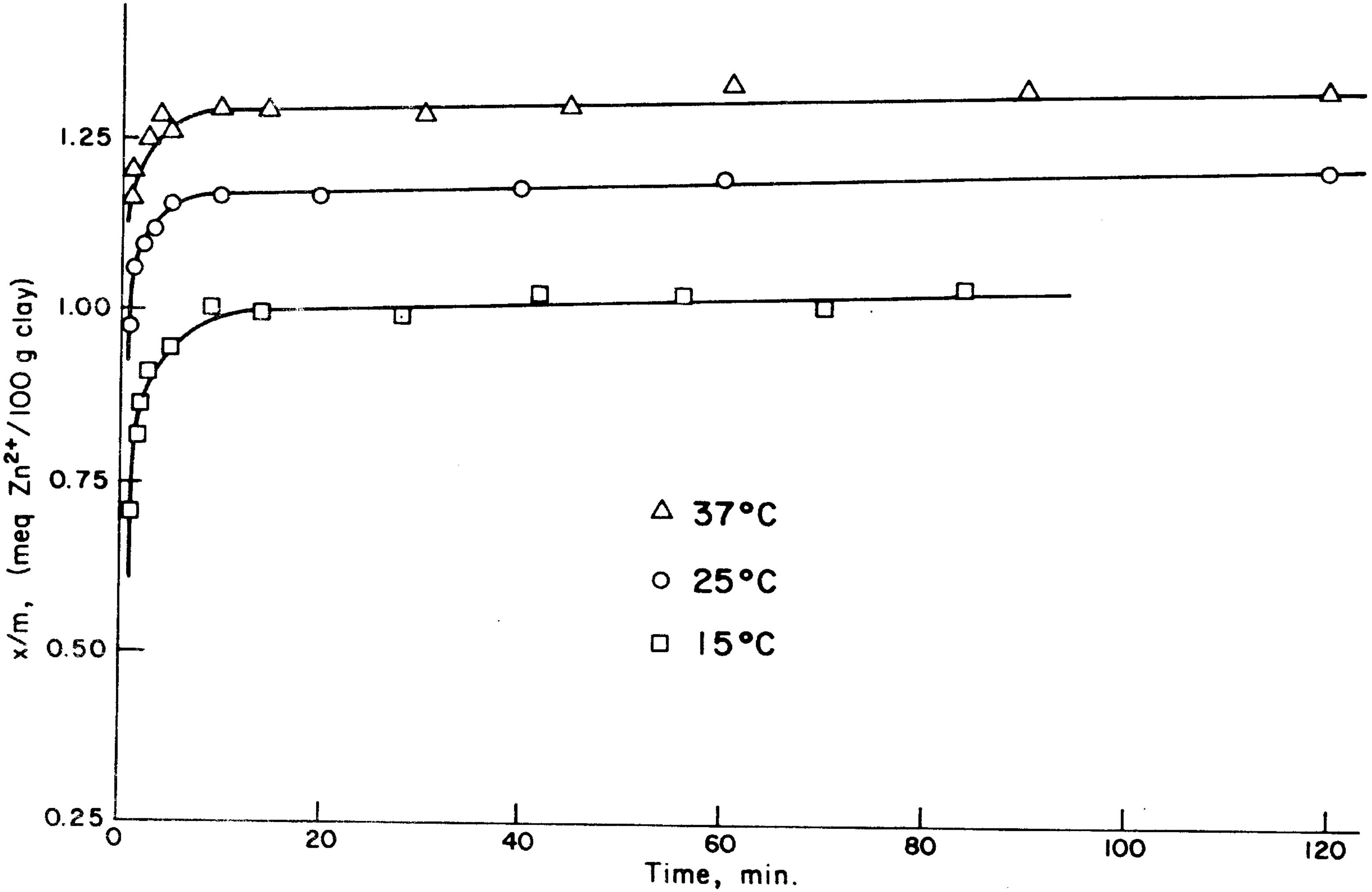

Figure 63. Effect of Temperature on the Uptake of Zn^{2+} by Illite

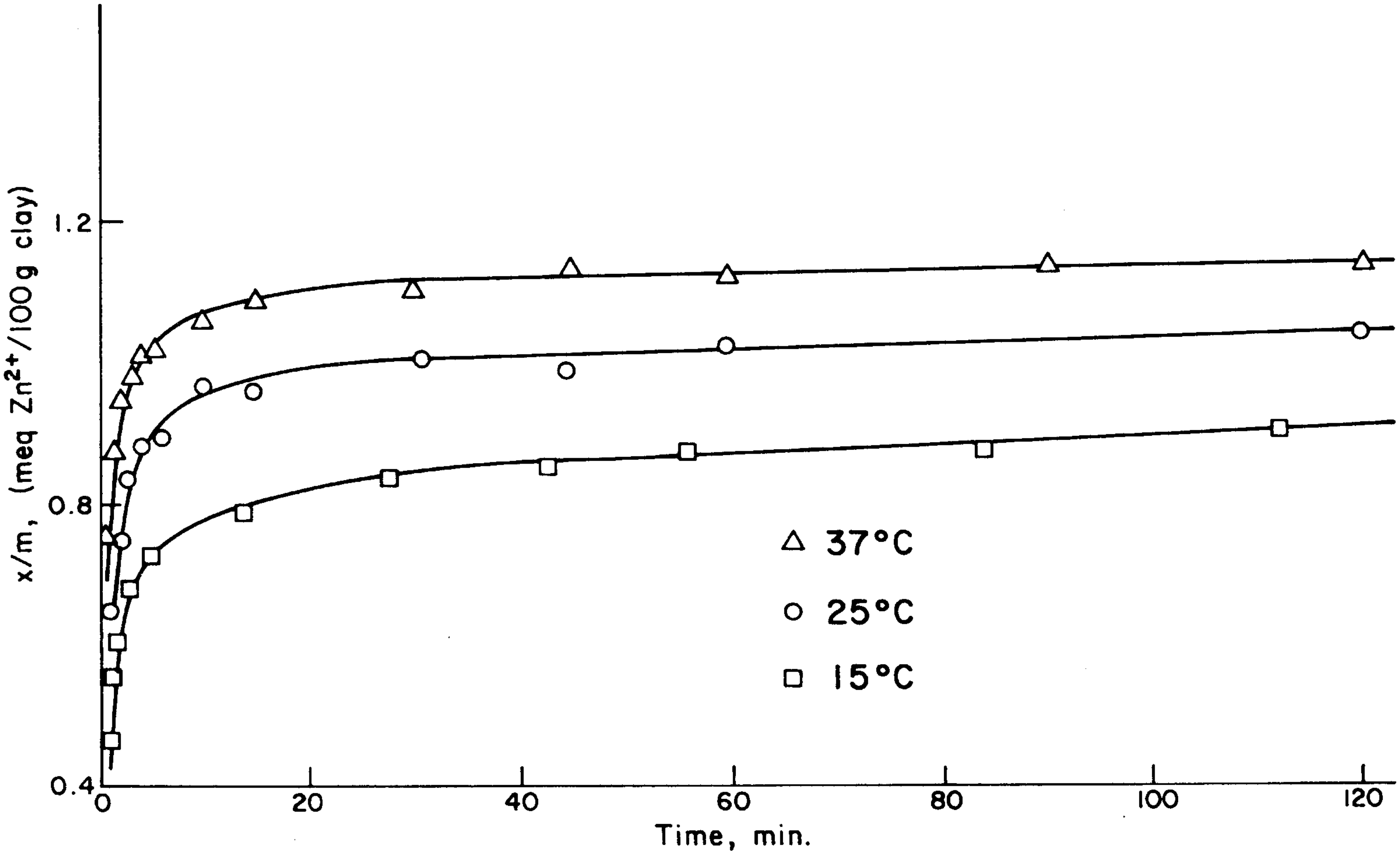

Figure 64. Effect of Temperature on the Uptake of Zn^{2+} by Montomorillonite

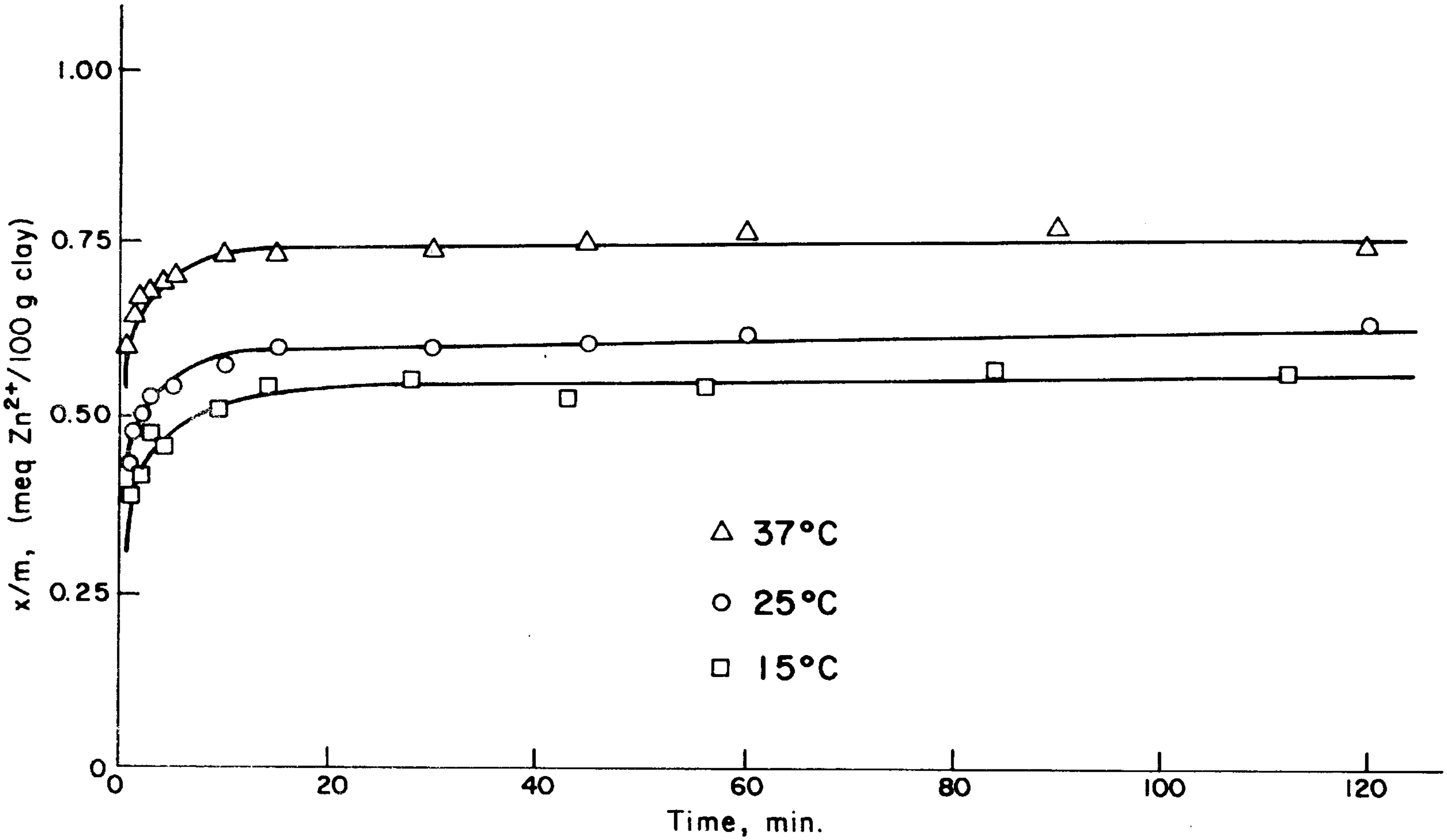

Figure 65. Effect of Temperature on the Uptake of Zn^{2+} by Kaolinite

result was obtained. Nevertheless, to look into the effect of temperature on the rate of the second step, the logarithm of the fraction of Zn^{2+} left in solution (expressed as ϕ) was plotted as a function of time (see Figures 66, 67 and 68). Since straight lines were found (for times greater than 20 minutes), the slopes were compared for three temperatures (Table 33). For all three clay samples the rate of the slow step was found to increase with temperature.

Table 33. Rate Constants of First-Order Kinetic Calculations for the Slow Uptake Step[1].

Temperature (C)	Illite k_1	Montmorillonite k_2	Kaolinite k_3
15	8×10^{-5}	11×10^{-5}	11×10^{-5}
25	9×10^{-5}	13×10^{-5}	13×10^{-5}
37	13×10^{-5}	16×10^{-5}	14×10^{-5}

[1] All slopes are expressed in sec^{-1}.

The rapidity of the uptake reaction suggests an ion-exchange or a complexation mechanism as opposed to physical adsorption. On the other hand, the slower rate of the second step possibly could be due to precipitation or to additional uptake by a physical adsorption mechanism. At the lower Zn^{2+} concentration (3.8×10^{-5} $\underline{M}$ Zn^{2+} or 2.5 mg Zn^{2+}/l) used in this experiment, precipitation can be ruled out as a possible explanation (Table 31). It is known that the rate of physical adsorption decreases with increasing temperature (McNeal, 1974), but Table 33 shows that the reverse is true here. Hence, the second step is probably a diffusion-controlled stage, with greater diffusion at the higher temperature due to greater thermal energy. This interpretation is consistent with the findings of other investigators.

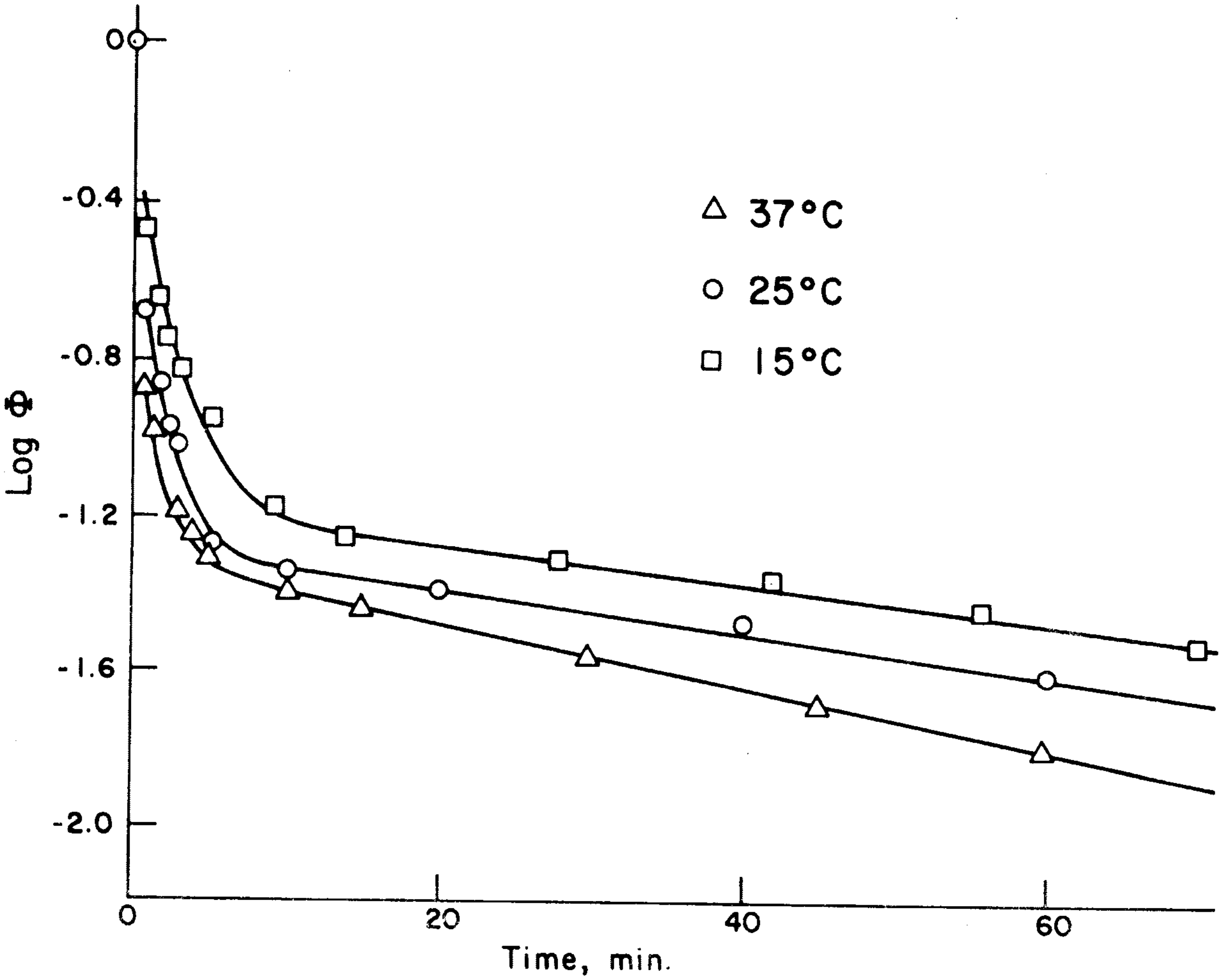

Figure 66. First Order Kinetic Plot in the Case of Illite

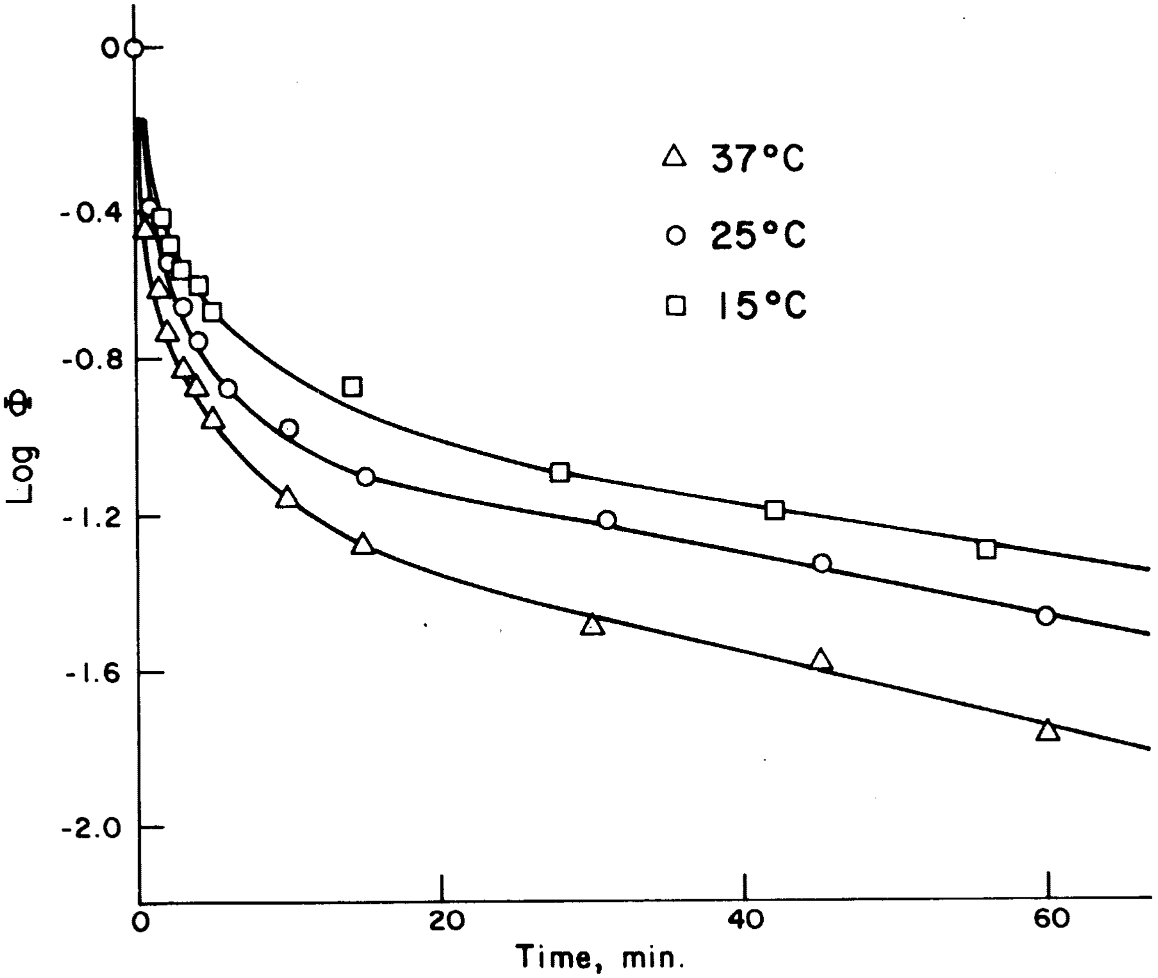

Figure 67. First Order Kinetic Plot in the Case of Montmorillonite.

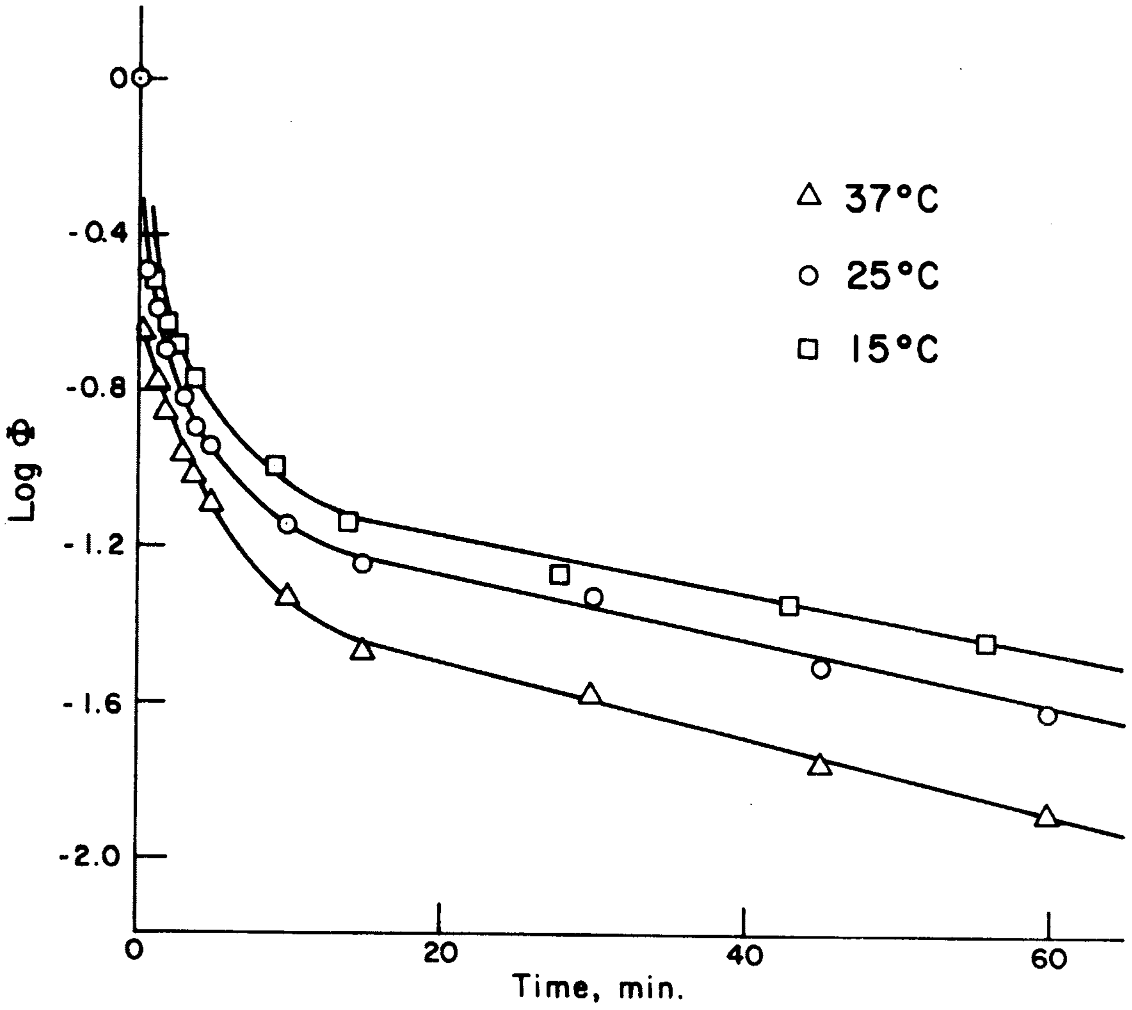

Figure 68. First Order Kinetic Plot in the Case of Kaolinite

Table 34. Freundlich Constants for the Adsorption of Zn^{2+} by Clay Minerals.

Sample	k (From Intercept)	n (From Slope)
Illite	-0.123	2.77
Montmorillonite	-0.277	2.57
Kaolinite	-0.586	2.18

Freundlich constants do not have any fundamental significance, but they are meaningful for comparative purposes. They are used by many workers (Bailey *et al.*, 1968; Helling *et al.*, 1971; Ping, 1972) as indexes of the adsorbing capacity of soils. The greater the constants, the greater the capacity. These constants are merely numbers which quantitate this adsorption for different adsorbent materials for identical experimental operations. This is illustrated by the results in Table 34, where we see that the decreasing order of Zn^{2+} uptake is illite, montmorillonite and kaolinite.

The same adsorption data did not obey the Langmuir adsorption equation

$$x/m = \frac{k_o SC}{1+kC} ,$$

where S = the maximum amount of adsorbate that can be adsorbed by the adsorbent, and k = an empirical constant.

By using the linear form of the equation

$$\frac{C}{x/m} = \frac{C}{S} + \frac{1}{k_o S} ,$$

a plot of

$$\frac{C}{x/m}$$

versus C did not yield straight lines for the three clay samples (Figure 69).

Effect of Clay Concentration

Figure 70 shows the total concentration of Zn^{2+} removed from the solution for various clay concentrations. The initial liquid-phase composition is the same for every data point on the graph: 3.06×10^{-5} M Zn^{2+} (or 2.0 mg Zn^{2+}/1), 0.010 M Cs^+ and 0.020 M TRIS. For each clay mineral, the concentration of solid material is the variable. In the case of kaolinite, the curve was not completed for lower values of clay concentration because in that range the standard deviation is too large. This happens for low adsorbed Zn^{2+} values because the uptake is measured by difference (by analyzing the Zn^{2+} left in solution).

If the removal of Zn^{2+} from the bulk of the solution were due to precipitation, the total uptake should appear as constant for low clay concentration. Figure 70 shows that the clays are involved in the Zn^{2+} behavior.

Effect of Ionic Strength

Since Cs^+ ions were added to the TRIS to keep the ionic strength constant in the fresh-water medium, they were used also to study the effect of ionic strength. Figure 71 describes the effect of changes in ionic strength (represented by the Cs^+ initial concentration) on the Zn^{2+} uptake (for an initial Zn^{2+} concentration of 3.06×10^{-4} M Zn^{2+} or 20 mg Zn^{2+}/1). The amount of Zn^{2+} adsorbed decreased with increasing

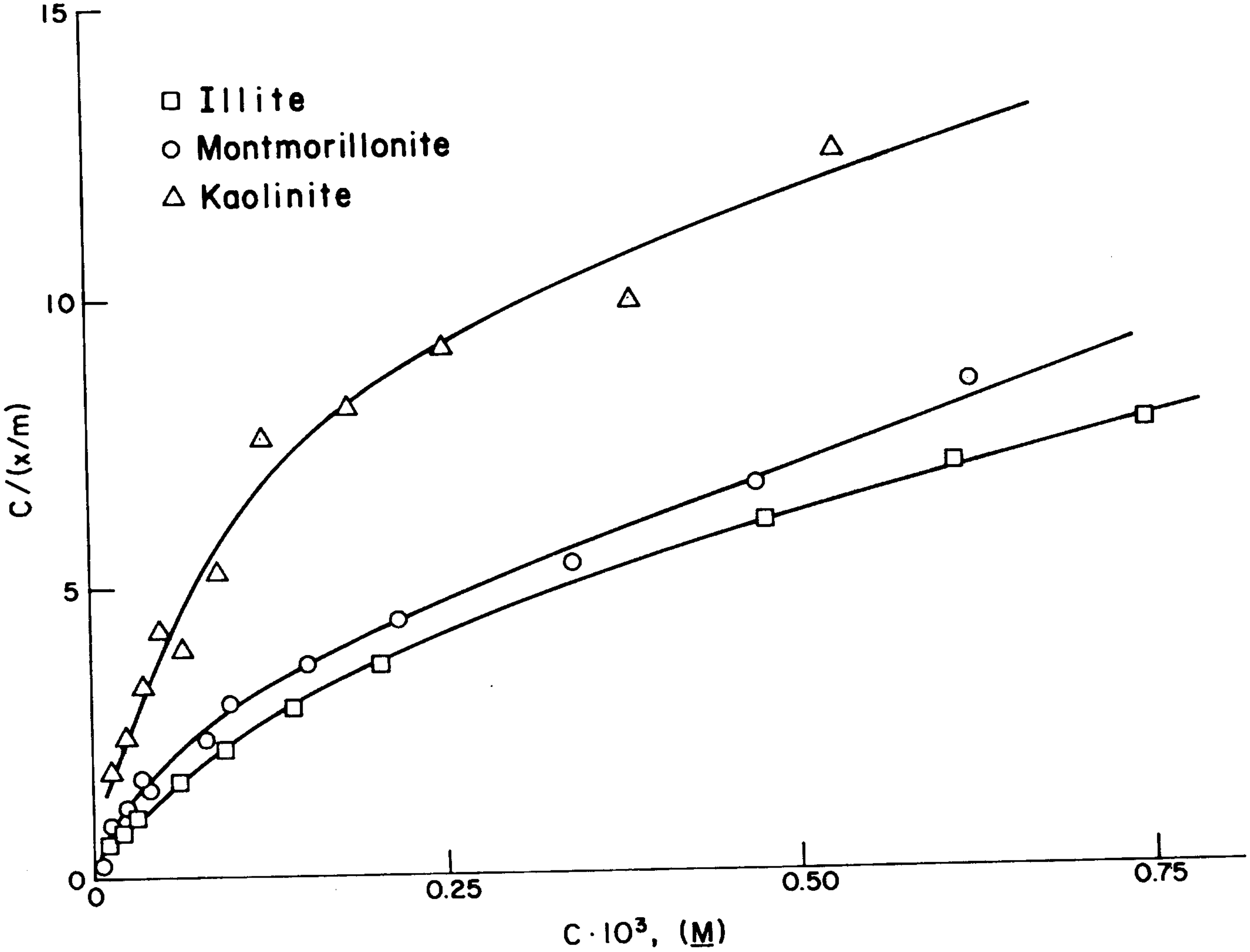

Figure 69. Langmuir Plot of Data for the Rapid Step of Uptake of Zn^{2+}

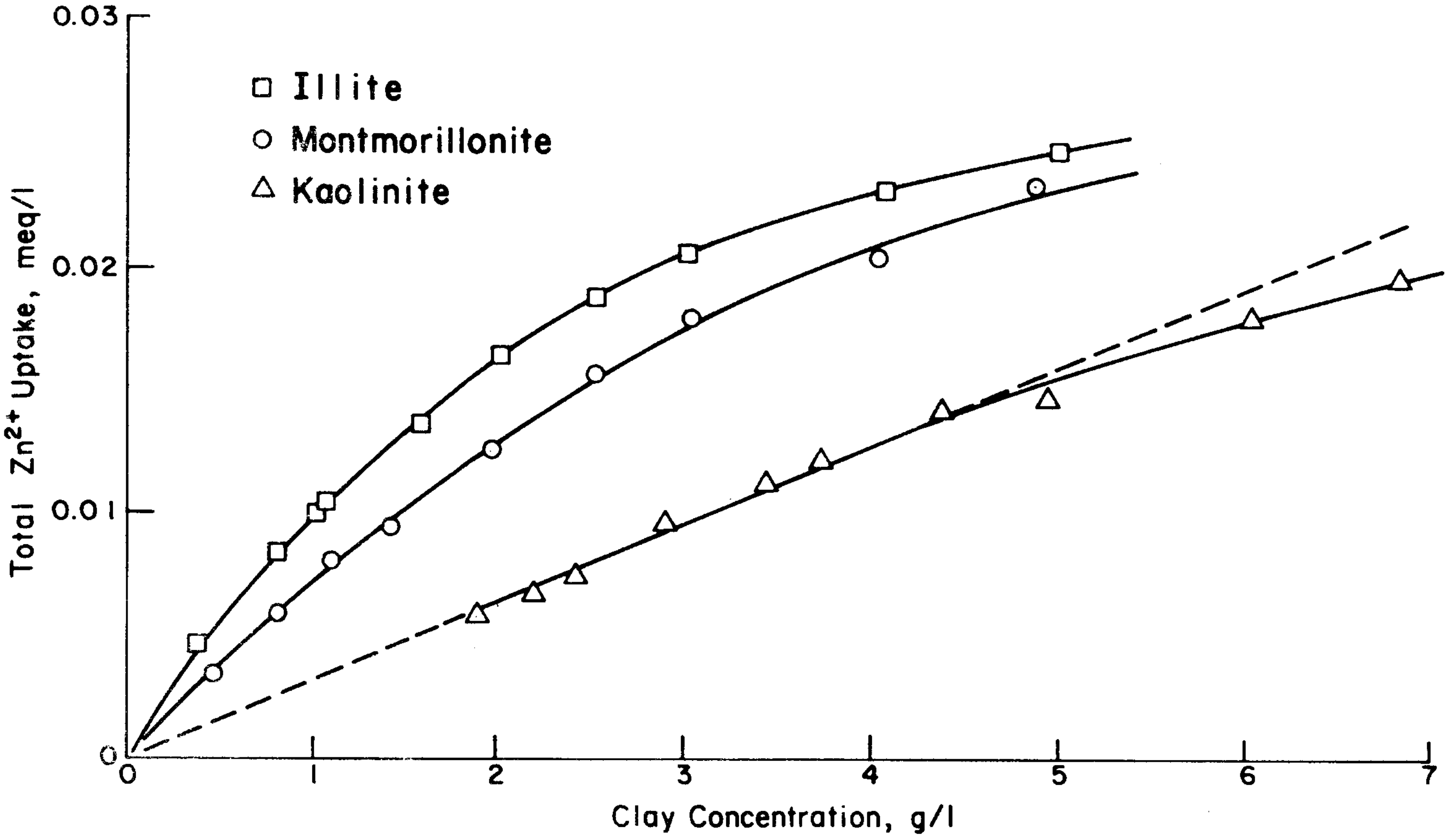

Figure 70. Total Uptake of Zn^{2+} as a Function of Clay Concentration

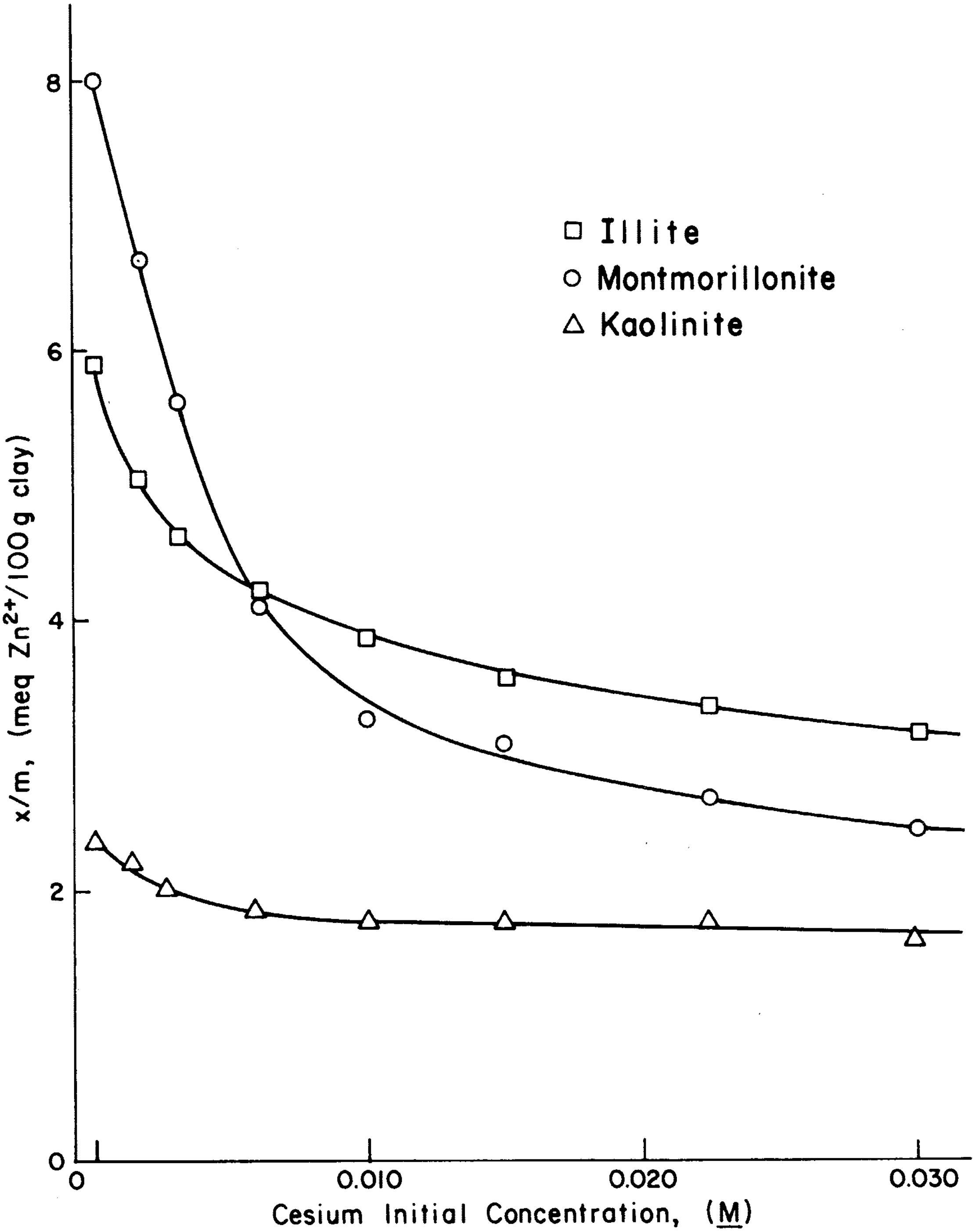

Figure 71. Uptake of Zn^{2+} as a Function of Cs^{+} Initial Concentration

ionic strength, which suggests increasing competition from Cs^+ ions. The magnitude of the variation depends upon the clay mineral.

To compare in a more quantitative manner the influence of Cs^+ concentration on the Zn^{2+} behavior in the three clay samples, a log-log plot of Zn^{2+} uptake as a function of the Cs^+ concentration was derived (Figure 72). The slope of the line for montmorillonite was greater than that for illite and kaolinite, which is indicative of a more efficient competition of Cs^+ with Zn^{2+} in montmorillonite than in illite and kaolinite.

When there was no Cs^+ present in solution, the Zn^{2+} uptake was greater for montmorillonite than for illite, which is a confirmation of the greater competition of Cs^+ with Zn^{2+} in montmorillonite than in illite. However, even in that case, the contribution of Zn^{2+} to the cation-exchange capacity of the clay was much smaller for montmorillonite (17%) than for kaolinite (42%) and illite (47%). Hence, the effect of Cs^+ is not large enough to explain the peculiar Zn^{2+} uptake capacity of montmorillonite. This is in support of either or both of the following arguments: the competition of TRIS with Zn^{2+} is greater in montmorillonite, and/or the adsorption of Zn^{2+} is privileged on illite and kaolinite. But because of the conclusions of the study of the effect of TRIS buffer (see below) we should retain only the last alternative.

The Cs^+ adsorption by the three clay samples also was observed and the results of this study are described in Table 35 for initial concentrations of zinc and cesium of 5×10^{-4} $\underline{M}$ and .010 $\underline{M}$, respectively. It is interesting to note that the amount of Cs^+ adsorbed corresponds to the whole CEC. But let us not forget that this capacity was determined by the NH_4^+ ion adsorption and that, hence, it has only a comparative

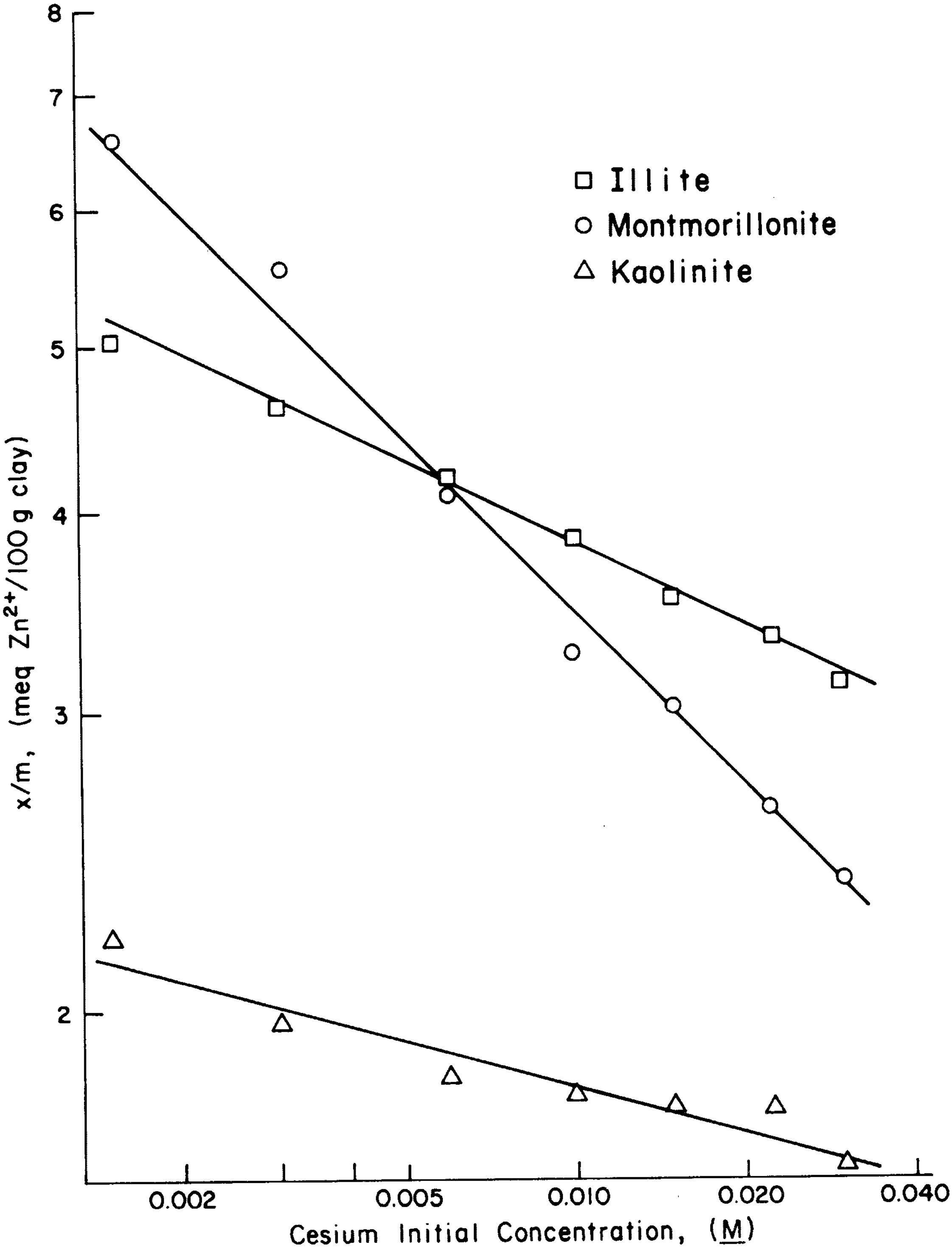

Figure 72. Log-log Plot of Uptake of Zn^{2+} as a Function of Cs^+ Initial Concentration

value. The uptake of Zn^{2+} does not follow the CEC pattern, suggesting that most of the negative charge density on montmorillonite is not available to this cation for neutralization.

Table 35. Uptake of Cs^{+} and Zn^{2+} by Three Clays[1]

Clay Sample	Adsorbed Zn^{2+}	Adsorbed Cs^{+}	Total Cation Adsorbed	CEC
Illite	5.0	12	17.0	12.4
Montmorillonite	4.5	47	51.5	47.4
Kaolinite	2.5	5	7.5	5.6

[1] All results are expressed as meq/100 g of clay.

Effect of TRIS

The effect of TRIS on the adsorption of zinc was determined by conducting experiments with different total TRIS concentrations (i.e., same pH but different amounts of TRIS present in solution). Table 36 shows that the influence of TRIS is of similar magnitude for all three clays, which suggests that TRIS is not responsible for the small Zn^{2+} uptake by montmorillonite as opposed to the value predicted by its CEC. Since the changes in Zn^{2+} uptake with varying TRIS concentration do not depend upon the clay sample, they can be due either to competition of TRIS with Zn^{2+} for adsorption or to complexation of Zn^{2+} with TRIS. It is probable that both mechanisms occur, but it was not possible to determine which one was predominant.

Summary of Results for Laboratory Study of Zn Uptake by Clays

The Zn^{2+} uptake by clay minerals in a fresh-water medium was studied and several physical and chemical parameters were investigated. Since interpretations of data concerning real systems are difficult to evaluate, a simple system was used to study the phenomenon of interest.

Experiments on the effect of the pH on Zn^{2+} uptake showed the importance of using a buffered system. The buffering action of the clays was found to occur in the decreasing order: illite, montmorillonite and kaolinite. The Zn^{2+} uptake increased with increasing pH for all three clays, but for illite and kaolinite this pH dependence was almost nonexistent at low pH.

The reaction of Zn^{2+} uptake was found to occur in two steps. The adsorption was very fast for 15 to 20 minutes, and afterward the reaction proceeded at a much slower rate. It was shown also that the Zn^{2+} uptake depended upon the temperature of the medium. The higher the temperature, the greater the amount of Zn^{2+} adsorbed.

Adsorption isotherms were plotted, and for the three clay samples they were found to obey the Freundlich equation. However, the amount of Zn^{2+} adsorbed in the presence of Cs^{+} cations and of TRIS buffer was not that expected from CEC values. The Zn^{2+} uptake occurred in the following decreasing order: illite, montmorillonite and kaolinite; whereas the CEC of montmorillonite was much greater than that of illite.

The effects of ionic strength and of several cations were investigated. The Zn^{2+} uptake was found to decrease with increasing ionic strength. For the alkali metal series, the competition with Zn^{2+} for adsorption on the clays was shown to increase with the atomic number. A similar effect occurred with the alkaline earth metals.

The exchangeability of adsorbed Zn^{2+} was studied by using Zn radionuclides as tracers. It was found that within the confidence level chosen (95%), all the Zn^{2+} adsorbed by the clays was in an exchangeable state. However, a small fraction (lower than 7%, 8% and 15% for illite, montmorillonite and kaolinite, respectively) could very well be irreversibly adsorbed, this restriction being due to the uncertainty of the measurements.

Summary of Conclusions for Zn^{2+} Uptake by Clay Minerals

The interpretation of the effects of various physical and chemical parameters on the Zn^{2+} uptake by clay minerals leads to the following conclusions. The rapidity of the reaction suggests either an ion-exchange or a chelation mechanism. The magnitude of the competition of alkali and alkaline earth metals rules out a significant contribution of binding of Zn^{2+} by chelation. These phenomena are those generally expected for a cation-exchange reaction. Increasing the concentration of other cations decreases the adsorption of Zn^{2+} due to competition. Also, the increasing preference for a given cation as one moves down the periodic table in a given group of elements can be explained by the fact that, for the smaller hydrated radius, the ion can be more closely, and hence more strongly, attached to the clay surface.

The significance of adsorption isotherms is limited, because here the system was not at equilibrium and, also, predictions for equilibrium concentrations higher than the range studied cannot be made. In other words, in this work a Freundlich isotherm does not necessarily eliminate the possible existence of specific adsorption sites.

Zinc cations are adsorbed mainly on the edges of the clay layers, which explains why the Zn^{2+} adsorption capacities of montmorillonite and illite, their structures being very similar, are of the same order of magnitude, whereas the CEC of montmorillonite is about four times greater than that of illite. But all three clays possess a non-pH-dependent Zn^{2+} adsorption capacity, indicating that some Zn^{2+} cations neutralize negative charges due to isomorphous substitutions, and thus are certainly situated between basal layers (probably mostly in irregularities of distorted crystal lattices). For kaolinite, it is not possible to ascertain whether these few cations are exchangeable or not because their contribution to the adsorbed Zn^{2+} content is of the order of magnitude of the standard deviation of the results of the exchange study. But for illite and montmorillonite it seems that not all the Zn^{2+} adsorbed between layers could be fixed irreversibly.

Ecological Implications of Zn^{2+} Uptake by Clays

In addition to the proposed interpretation of the mechanism of Zn^{2+} uptake, it is important to consider the ecological implications of changes in physical and chemical conditions in natural waters.

The most important parameter of any system, in our case, appears to be the hydrogen ion concentration. Not only may acid mine drainage basins bring an important load of Zn^{2+} into streams, but the low pH of the water does not favor its adsorption on the suspended particles.

The clay fraction of suspended particles and bottom sediments of streams and lakes acts as a buffer reservoir for the Zn^{2+} present in natural waters. If there is a sudden input of Zn^{2+} into a system, the amount of cation adsorbed by the clay minerals will increase. On the other hand, if the Zn^{2+} concentration decreases (by dilution at a confluence, for example), some Zn^{2+} will be desorbed from the suspended load. Thus, to a certain extent, the Zn^{2+}-clay system controls the Zn^{2+} concentration in the soluble phase of natural waters.

Suspended particles are certainly more efficient than bottom sediments for Zn^{2+} adsorption because of greater availability and large surface area, and also because the pH of the latter is often lower than that of the surrounding water. Thus, because of faster currents, rivers, more than lakes and oceans, are able to carry Zn^{2+} in the adsorbed state. As one goes downstream, the ionic strength usually increases, providing Zn^{2+} with an increasing number of competitors for adsorption. At the mouth of a river, when the stream enters the sea, which is of much higher ionic strength, there is a well known effect of desorption of heavy metals (Turekian, 1971).

Since Zn^{2+} is adsorbed less in hard water than in soft water, it is more available to aquatic organisms in streams with a high dissolved salt content. But, on the other hand, its action is masked by a greater amount of other cations, and according to most laboratory bioassays this last effect appears to predominate over the first one.

The temperature has only a small effect on the Zn^{2+} uptake, this cation is adsorbed less in winter, when there is less biological activity in aquatic ecosystems.

This study is somewhat limited because only the divalent cationic form of Zn was studied. Nevertheless, these results are fully applicable to ^{65}Zn (whose increasing abundance is a cause for great concern) because this radionuclide is believed not to be organically bound in natural waters (Duursma, 1972).

The understanding of transport mechanisms in environmental systems is of great importance. There are two principal routes of action to study such phenomena. The first possibility consists of the accumulation of data from natural systems to deduce transport mechanisms. The second possibility is the direct study of the mechanism and the cautious application of the conclusions to real systems. This last method was chosen for this work, but both ways have their place in research.

IV. Upper Spokane River

A. Water Quality

Five of the original six water quality stations sampled in our Title I project were maintained in this study and two were added (Figures 1 and 73) to verify further the results of our earlier study. In addition to standard water quality tests, additional parameters such as algae identification and enumeration, total organic carbon (TOC), chlorophyll analysis and in some instances Carbon 14 techniques were employed in an attempt to understand whether the upper Spokane River is responding to a nutrient influx or if its productivity is significantly affected by high metallic content. Appendix D contains a summary of the data collected.

Temperature

Water temperatures began a steady decline from 16 C in October 1972 to 2 C at several sampling sites in early January 1973. Temperatures rose slightly in February and began an upswing in early March which continued until maximum summer temperatures of 27 C were reached at several stations by 1 August 1973. Composite temperatures and rate of discharge at the Post Falls Station are shown in Figure 74. These patterns are consistent with the results of our earlier study, with the notable exception of January to April of 1974. This was a period of flooding in the Coeur d'Alene region, which resulted in record high flows in the Spokane River.

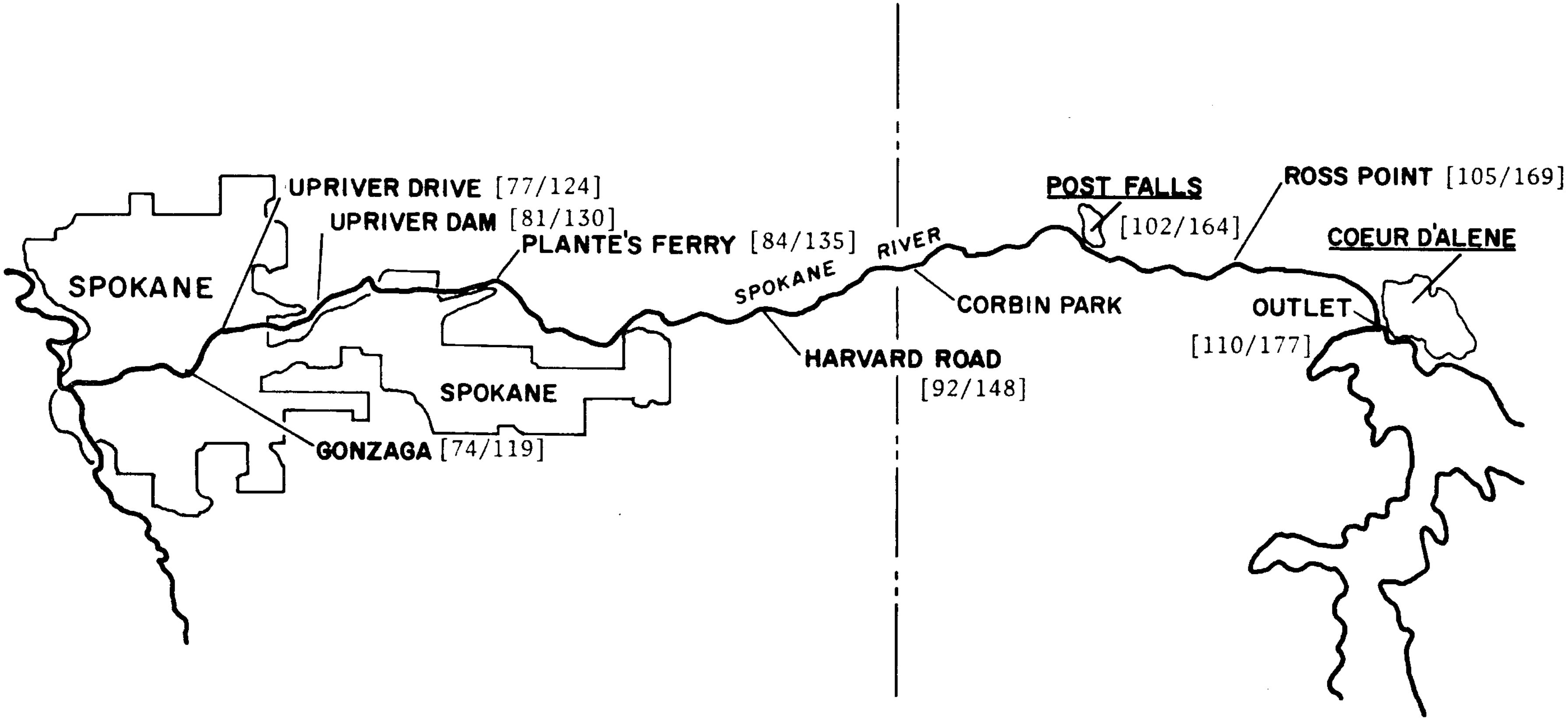

Figure 73. Sampling Stations on the Spokane River (Figure in Brackets Represents River Mile/Kilometer from Mouth of Spokane River).

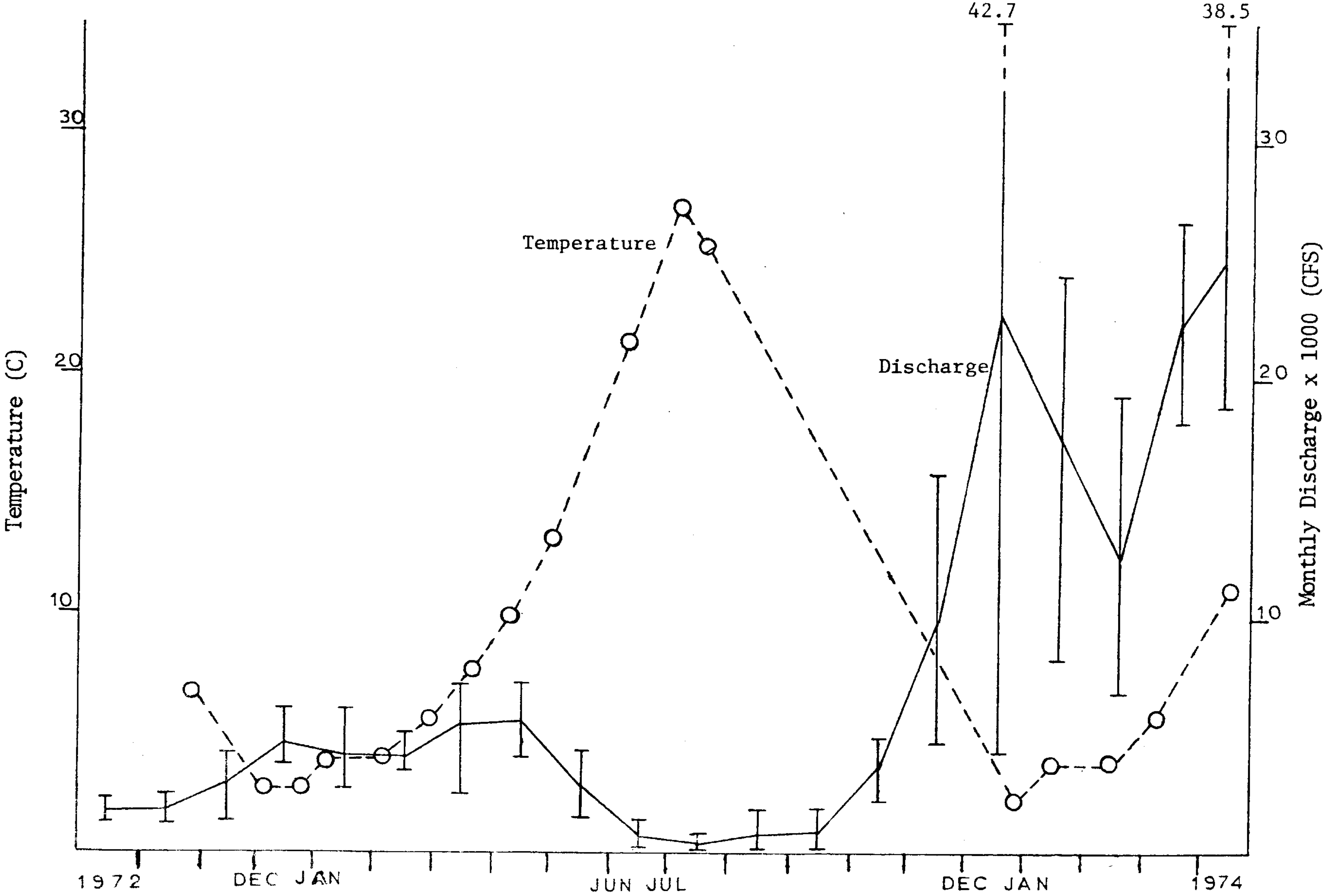

Figure 74. Spokane River Flow and Temperature at Post Falls, Idaho

Dissolved Oxygen

The dissolved oxygen content of the upper Spokane River generally is indicative of the good condition (relatively free of organic wastes) of this portion of the river. Periphyton and aquatic weed growth in the lower region of the study area (Plantes Ferry to Gonzaga) no doubt contributes to the 105-110% saturation measurements made during the summer period. Correspondingly, there is a relatively low biochemical oxygen demand (BOD) made upon the waters of this river. In fact, it rarely rises above 2.0 mg/l (5- to 10-day BOD laboratory measurements extrapolated to standard 5-day BOD). On the other hand, there are indications that some domestic or industrial disposal occurs in the river. Chemical oxygen demand (COD) on many occasions almost doubles at the lower four sampling stations (Plantes Ferry, Upriver Drive, Upriver Dam and Gonzaga).

Nutrients

Prime nutrients such as orthophosphorus, ammonia and nitrate nitrogen, were present in relatively low quantities throughout the sampling period. A general observation might be made that nitrates usually increased with the downstream movement of the water toward the city of Spokane. Phosphorus and the other forms of nitrogen measured did not (Appendix D). Bannon (1974) applied statistical analysis to the data collected during 1973-74 and found that nitrate and orthophosphate in relation to location show a highly significant (1%) and a significant relation (5%), respectively. Data means are shown in Figures 75 and 76. Two major nutrient peaks occur, one during the low-flow period and another during the high-flow period (Figures 77 and 78). Analysis of

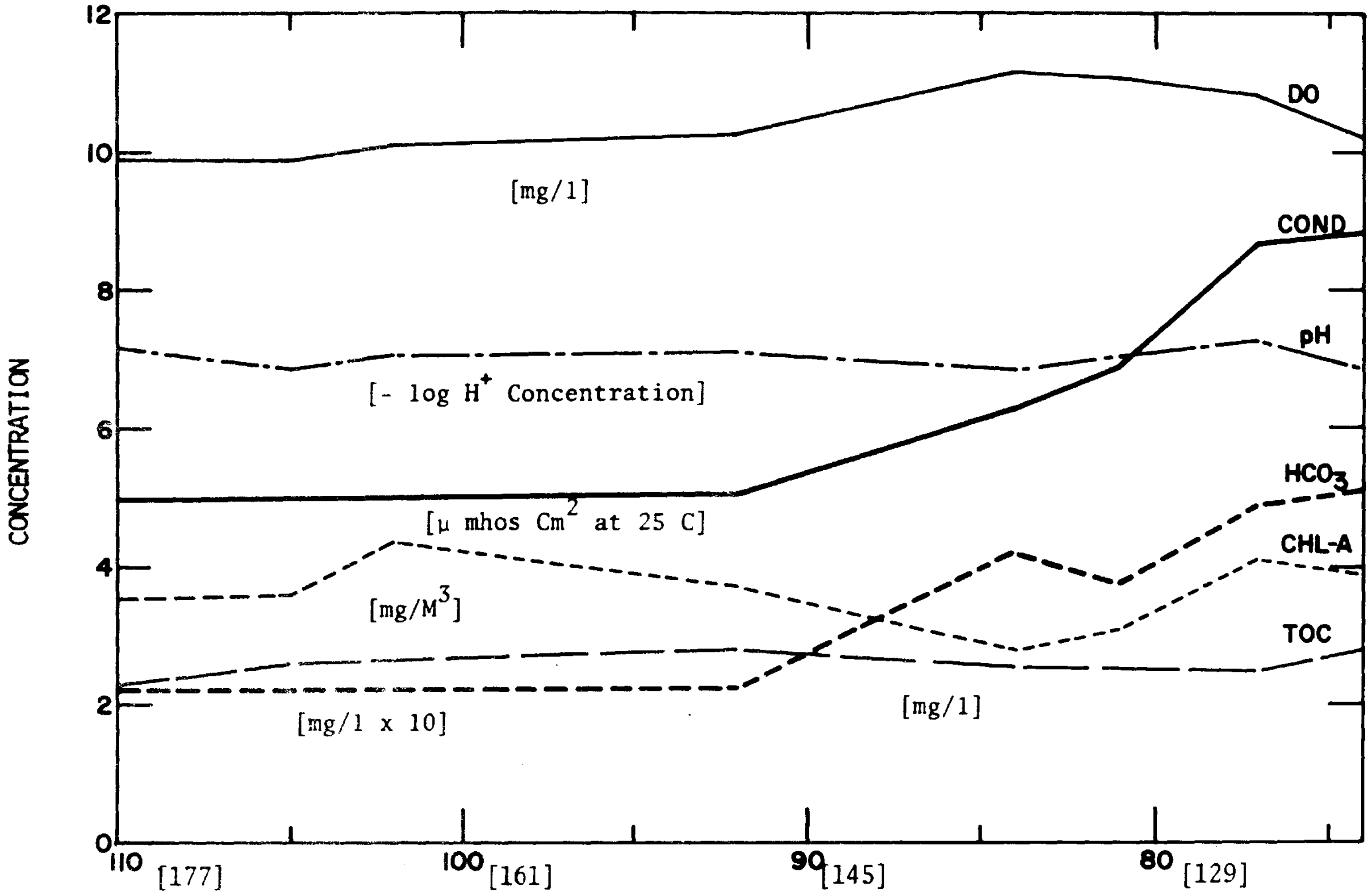

Figure 75. Physicochemical Measurement Means by River Mile [Kilometer].

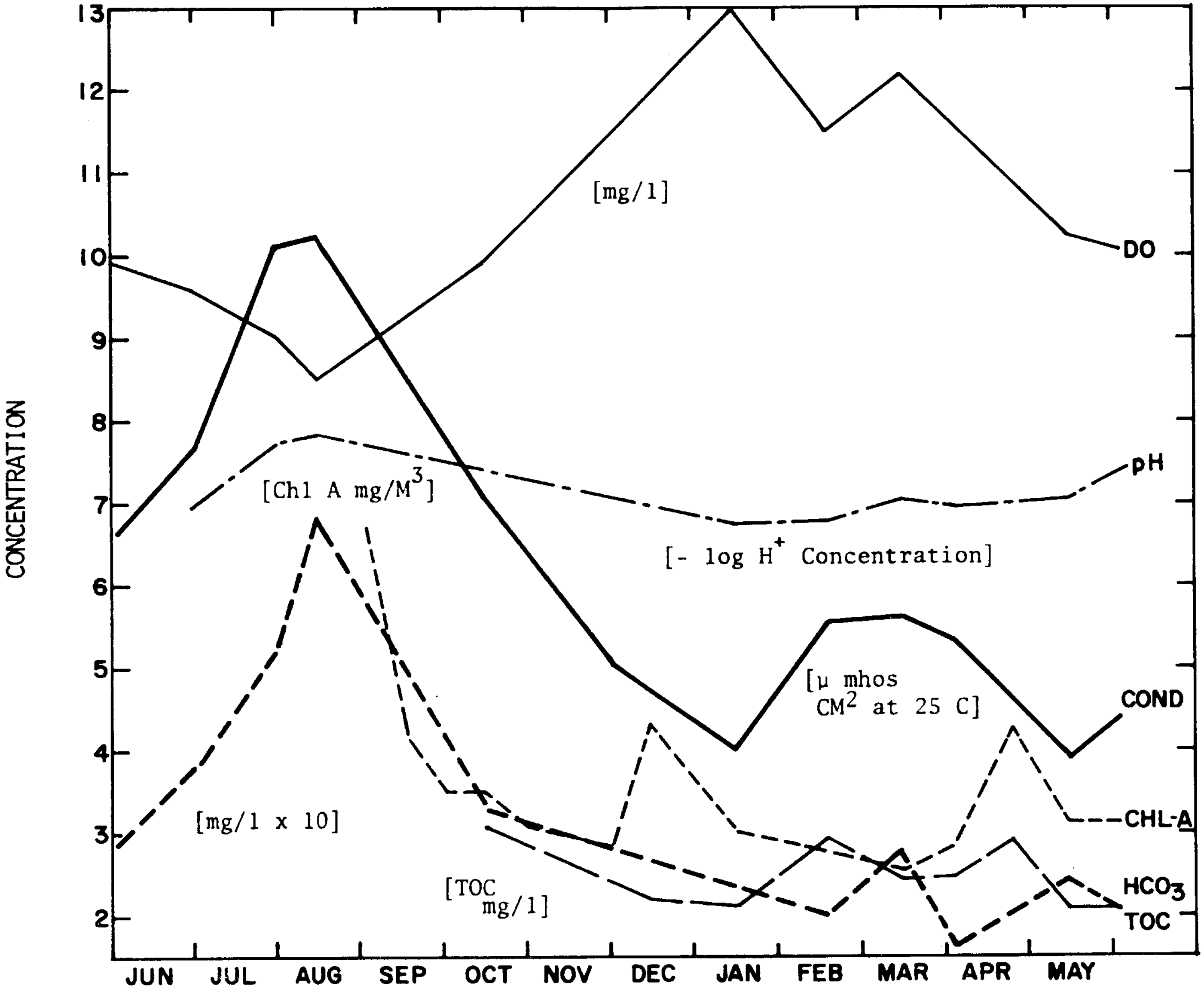

Figure 76. Physicochemical Measurement Means by Date

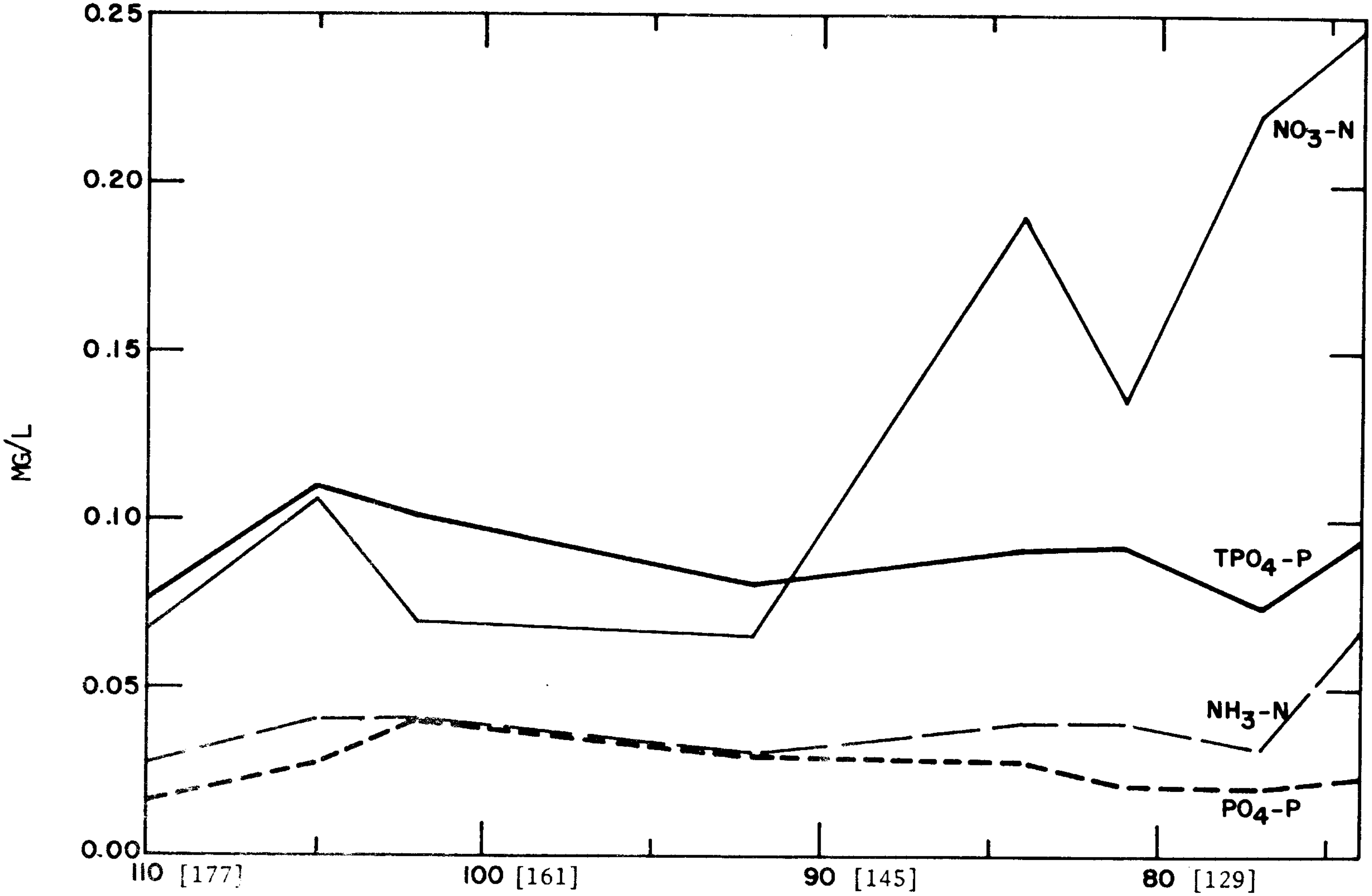

Figure 77. Mean Concentration of Nutrients by River Mile [Kilometer]

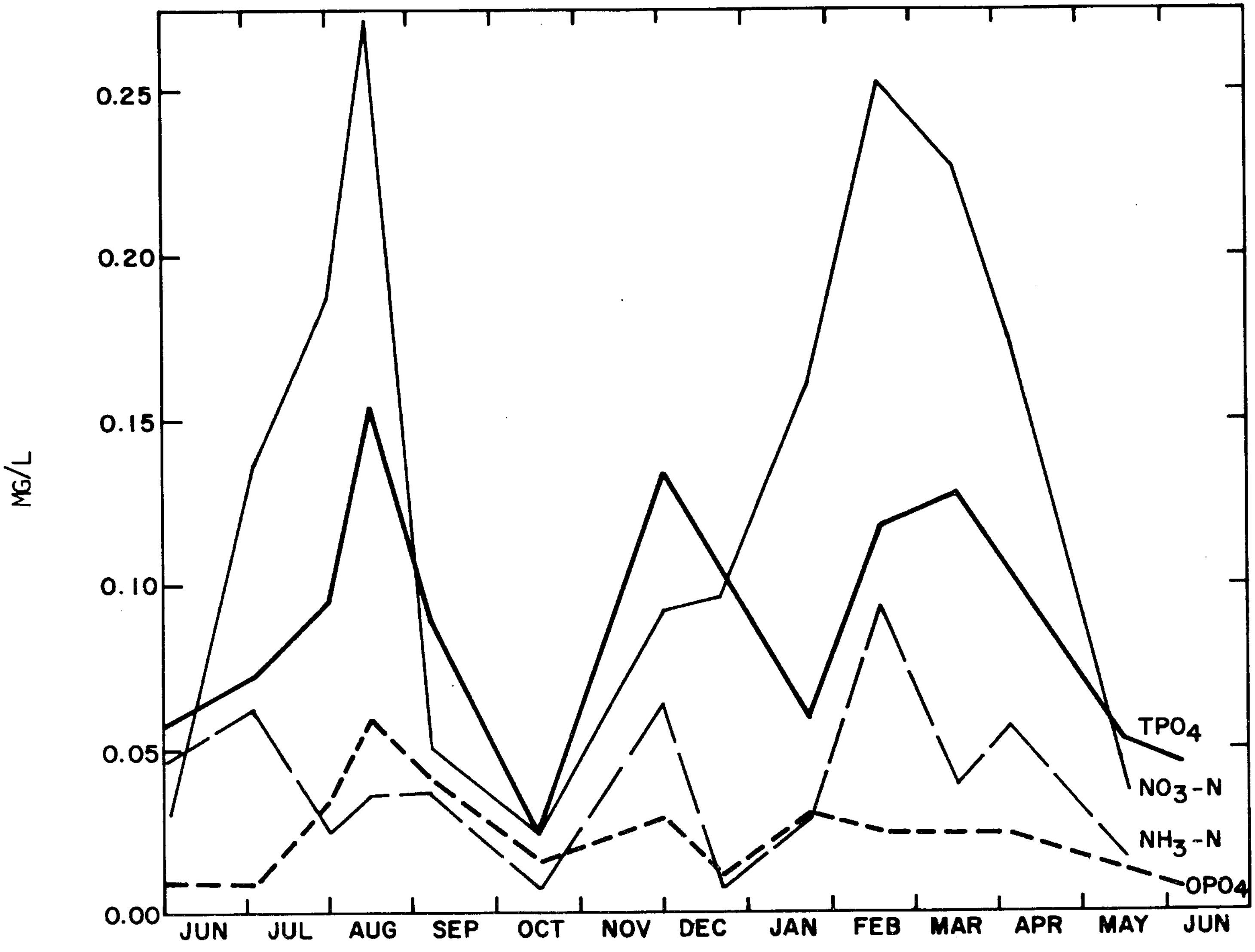

Figure 78. Mean Concentration of Nutrients by Date

variance tests indicates that all the nutrients tested (ortho- and total phosphorus) as well as nitrogen constituents show this trend at the 1% level except ammonia, which was significant at the 5% level. Bannon (ibid.) also measured total organic carbon in the upper Spokane River as a part of this investigation and found no significant difference among stations. However, it was impossible to study the effect of low flow because of the manufacturer's inability to deliver testing equipment on time, combined with the constraints imposed by the investigation's funding period. Measurements of periphyton and phytoplankton growth suggested by this and our earlier study indicate that a difference among stations can be expected. Unfortunately, record-high river flow during the spring and early summer of 1974 again negated our efforts to accurately verify this phenomenon. It is interesting to note that, in addition to carrying off or severely abrading our invertebrate samplers and traps, brick slide and basket periphyton containers, the river also threatened the 1974 World Environmental Exposition site in Spokane proper.

Metallic Constituents in the Spokane River

Atomic absorption analysis of certain metallic elements in the Spokane River was carried out at seven and on occasion at eight of the water quality stations on a monthly basis. The results shown in Table 36 are similar to those of our earlier study (OWRR, B-044 WASH and B-015 IDA).

Table 36. Atomic Absorption Analysis of Selected Metallic Elements in the Spokane River.[1]
(Expressed as μg/l)

Date Metal	Lake Outlet	Ross Point	Post Falls	Harvard Road	Up River Dam	Up River Drive	Gonzaga
8-30-72							
Cd	-	3.4	2.4	0.8	0.7	-	-
Cu	-	0.5	0.5	0.5	0.2	-	-
Fe	-	0.7	0.4	1.0	0.4	-	-
Pb	-	3.0	3.0	-	-	-	-
Zn	-	109.0	117.0	78.0	80.0	-	-
11-9-72							
Cd	2.4	2.7	2.0	3.0	2.9	-	1.7
Cu	1.9	1.4	1.1	0.7	1.0	-	0.8
Fe	2.6	1.9	2.7	2.2	1.2	-	0.8
Pb	2.0	2.0	2.0	2.0	-	-	-
Zn	185.0	189.0	183.0	166.0	155.0	-	126.0
11-22-72							
Cd	4.0	2.8	1.8	3.6	3.8	3.6	1.4
Cu	0.5	0.3	0.3	0.3	0.6	0.8	0.5
Fe	3.6	2.8	2.7	2.7	3.0	2.0	2.6
Pb	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Zn	202.0	208.0	220.0	205.0	174.0	127.0	140.0
1-4-73							
Cd	1.8	2.2	4.2	2.8	3.1	2.3	3.4
Cu	0.9	0.7	0.8	0.5	0.5	0.6	0.6
Fe	4.8	5.0	3.5	3.2	2.2	2.4	3.5
Pb	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Zn	225.0	215.0	225.0	225.0	215.0	210.0	210.0
2-2-73							
Cd	2.6	1.7	2.1	2.0	2.7	1.6	1.4
Cu	0.8	1.0	0.8	1.0	0.5	0.5	0.7
Fe	6.0	6.0	3.5	6.0	2.0	3.0	5.0
Pb	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Zn	240.0	240.0	240.0	240.0	230.0	230.0	220.0

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[1] Waters analyzed were passed through .45μ filters.

Table 36 Continued

Date Metal	Lake Outlet	Ross Point	Post Falls	Harvard Road	Up River Dam	Up River Drive	Gonzaga
3-3-73							
Cd	2.3	2.2	2.3	2.2	2.3	2.2	2.0
Cu	1.0	0.8	0.5	0.7	0.5	0.9	0.7
Fe	9.2	7.5	8.8	6.0	6.4	7.2	6.0
Pb	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Zn	260.0	270.0	270.0	270.0	270.0	220.0	235.0
4-5-73							
Cd	2.1	2.0	2.2	2.2	2.0	1.8	2.5
Cu	0.9	0.5	0.9	1.2	1.1	0.8	2.5
Fe	14.0	12.0	12.0	18.0	11.0	14.0	11.0
Pb	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Zn	250.0	252.0	285.0	273.0	267.0	250.0	236.0
5-8-73							
Cd	1.8	2.5	3.9	3.3	3.3	2.5	2.5
Cu	0.5	0.3	0.7	0.6	0.6	0.5	0.5
Fe	40.0	28.0	33.0	30.0	23.0	29.0	28.0
Pb	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Zn	219.0	266.0	273.0	270.0	276.0	258.0	250.0
6-6-73							
Cd	3.0	3.2	2.7	3.0	2.9	2.6	2.4
Cu	0.4	1.1	0.5	0.5	0.5	0.8	0.5
Fe	2.0	2.5	1.0	1.0	1.0	1.0	1.0
Pb	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Zn	354.0	306.0	300.0	295.0	214.0	210.0	212.0
7-6-73							
Cd	2.0	2.2	-	2.9	2.5	2.5	1.5
Cu	1.3	0.8	0.5	0.9	1.1	0.7	0.8
Fe	5.0	1.0	3.0	1.0	1.0	1.0	1.0
Pb	5.0	5.0	2.0	3.0	9.0	4.0	12.0
Zn	344.0	338.0	331.0	336.0	221.0	218.0	216.0

Table 36 Continued

Date Metal	Lake Outlet	Ross Point	Post Falls	Harvard Road	Plantes Ferry	Up River Dam	Up River Drive	Gonzaga
8-1-73								
Cd	2.5	2.2	3.4	5.2	-	1.2	1.9	-
Cu	0.5	0.8	0.6	0.7	-	1.4	1.1	-
Fe	1.0	2.0	3.0	1.5	-	1.5	1.0	-
Pb	2.0	2.0	2.0	2.0	-	2.0	2.0	-
Zn	294.0	267.0	262.0	250.0	-	219.0	212.0	-
8-16-73								
Cd	4.2	1.6	1.1	2.0	2.3	-	1.2	5.3
Cu	1.5	0.8	0.4	0.8	1.3	-	1.4	1.8
Fe	1.0	1.5	2.0	2.0	1.0	-	2.0	2.0
Pb	2.0	2.0	2.0	2.0	2.0	-	2.0	2.0
Zn	225.0	215.0	215.0	210.0	230.0	-	211.0	210.0
9-7-73								
Cd	1.9	2.1	1.3	1.3	2.3	2.1	0.9	1.3
Cu	1.4	1.3	1.3	1.6	1.4	1.8	2.1	2.7
Fe	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Pb	2.0	2.0	2.0	3.0	3.0	2.0	2.0	2.0
Zn	189.0	214.0	218.0	198.0	199.0	153.0	155.0	150.0
Ag	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
10-16-73								
Cd	1.7	4.1	1.3	1.1	-	0.4	3.8	0.4
Cu	0.1	0.1	0.3	0.4	-	0.5	0.3	0.4
Fe	2.0	1.0	8.0	1.0	-	7.0	1.0	7.0
Pb	2.0	2.0	2.0	2.0	-	2.0	2.0	2.0
Zn	218.0	272.0	266.0	270.0	-	273.0	258.0	245.0
Ag	0.2	0.2	1.0	1.0	-	1.0	0.2	1.0
12-18-73								
Cd	4.3	3.1	2.9	1.6	1.3	1.3	1.2	1.5
Cu	0.9	0.1	0.1	0.3	0.3	0.1	0.1	0.9
Fe	8.0	7.0	3.0	6.0	5.0	10.0	7.0	4.0
Pb	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Zn	422.0	353.0	355.0	290.0	245.0	287.0	277.0	281.0
Ag	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2

Table 36 Continued

Date Metal	Lake Outlet	Ross Point	Post Falls	Harvard Road	Plantes Ferry	Up River Dam	Up River Drive	Gonzaga
1-23-74								
Cd	3.2	3.3	3.5	3.7	3.8	1.7	3.1	4.8
Cu	2.0	1.2	1.3	1.5	1.5	1.3	1.9	1.5
Fe	20.0	16.0	20.0	20.0	22.0	12.0	20.0	24.0
Pb	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Zn	444.0	382.0	349.0	367.0	386.0	345.0	336.0	331.0
Ag	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
2-26-74								
Cd	2.6	2.5	2.3	2.9	2.3	2.3	2.4	2.4
Cu	2.5	2.8	2.8	3.7	2.6	2.9	2.8	4.0
Fe	35.0	41.0	37.0	34.0	36.0	25.0	26.0	23.0
Pb	12.0	16.0	14.0	12.0	12.0	9.0	9.0	9.0
Zn	641.0	581.0	462.0	429.0	420.0	441.0	402.0	443.0
Ag	0.2	0.3	0.3	0.3	0.2	0.3	0.2	0.3

Bacteria

Bacterial quality of the Spokane River is classified as "good" but does not meet the present A classification set forth by the Washington State Department of Ecology (1973). Coliform counts at the Cedars station (Coeur d'Alene Lake outlet) were the lowest of all stations, with a mean count of 31 per 100 ml (Tables 37 and 38), and periods of high coliform counts (9/7/73, 2/26/74) did not show correspondingly high fecal coliform counts. Total coliforms increase downriver at the Ross Point and Post Falls stations to 240 and 475 per 100 ml, respectively. Fecal coliforms show a corresponding increase at these stations. Bacterial counts slightly decline at the Harvard Road station and then increase from the Upriver Dam station to the Gonzaga station. This pattern has been consistent since 1971 (Funk, Rabe, Filby *et al.*, 1973). The large increase in numbers of total coliforms at Post Falls and Ross Point stations indicates surface runoff in this area or possibly regrowth of bacteria from the Coeur d'Alene city treatment plant. R values (R = fecal coliform/fecal streptococcus) of less than four at these stations suggest the increase is not due to raw human effluent. R values decrease to .7 and .1 respectively at the Harvard Road and Plantes Ferry stations and indicate bacteria of mainly animal origin. The R value increases at the Gonzaga station to 5.1.

The Spokane River, according to our data, meets Washington State Class A standards (median of 240 or less total coliforms with 20% of the samples less than 1000) at Cedars, Harvard Road and Plantes Ferry stations. Other sections of the river meet Washington State Class B standards (median values of 1000 or less total coliforms per 100 ml with less than 10% of the samples greater than 2400).

Table 37. Bacteria of Water Quality Significance in the Upper Spokane River. 1972-1974.

TC(FC)FS[R] [1]

Station (RM/K)[2]	11/22/72	1/4/73	3/3/73	4/6/73	5/8/73
Cedars (110/177)	~10(~0)~0[0]	~10(~0)~0[0]	60(~0)~0[0]	~40(22)~0[>1]	~22(~0)~3[<1]
Ross Point (105/169)	~910(~133)41[3]	3000(~369)~162[2.3]	2200(~226)~115[2.0]	~10(~4)~0[>1]	~5770(~699)~153[4.4]
Post Falls (102/164)	510(84)~1[84]	~900(~236)66[3.6]	~2040(190)~96[2.0]	440(94)~11[8.5]	2430(~256)~125[2.0]
Harvard Road (92/148)	210(~13)~1[13]	460(~101)38[2.7]	200(~12)~6[2.0]	~10(~0)~0[0]	200(49)33[1.5]
Plantes Ferry Park (84/135)					
Upriver Dam (81/130)	~100(~4)~3[1.3]	1800(~170)42[4.0]	700(74)20[3.7]	~0(~0)~0[0]	~1900(~1)~14[.1]
Upriver Drive (77/124)	~60(~1)~3[.3]	2400(~164)52[3.2]	310(~34)~7[4.9]	~10(~0)~0[0]	~2370(~0)~6[<1]
Gonzaga (74/119)	270(89)~10[9]	4300(~443)~147[3.0]	420(38)~6[6.3]	~0(~0)~2[<1]	~1690(~385)41[9.4]

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[1] TC = Total Coliform/100 ml
FC = Fecal Coliform/100 ml
FS = Fecal Streptococci/100 ml
R = FC/FS

[2] RM/K = River Mile/Kilometer

TC(FC)FS[R]

Table 37 Continued

Station (RM/K)	6/4/73	7/6/73	8/1/73	8/16/73	9/7/73
Cedars (110/177)	~8(~4)~0[<1]	~0(~1)~0[>1]	~600(~140)~0[1]	- (~10)20[.5]	~1200(~2)~20[.1]
Ross Point (105/169)	~80(52)-[-]	~10(~4)~0[>1]	- (~6)25[.24]	- (~2)~11[.2]	~4800(~12)~14[.9]
Post Falls (102/164)	40(12)4[3]	~180(~6)~0[>1]	~870(~0)~0[0]	- (~0)~9[<1]	~9000(~6)~8[.8]
Harvard Road (92/148)	~40(~13)~7[1.9]	~0(~5)~0[>1]	620(~0)~0[0]	- (~2)36[.05]	~1800(~12)~98[.1]
Plantes Ferry Park (84/135)				- (~4)~4[1.0]	TNTC(~22)~280[.08]
Upriver Dam (81/130)	- (26)33[.8]	10(0)0[0]	410(~10)~0[>1]	- (40)TNTC[<1]	~12600(~4)~120[.03]
Upriver Drive (77/124)	~30(~11)~15[.7]	~10(~4)~1[4]	460(~50)~37[1.4]	- (~4)~2[2]	~7800(~6)72[.08]
Gonzaga (74/119)	~80(108)~11[9.8]	560(~452)~0[>1]	550(~0)~0[-]	- (~2)~13[.15]	TNTC(18)28[.6]

TC(FC)FS[R]

Table 37 Continued

Station (RM/K)	11/14/73	12/18/73	1/23/74	2/26/74	3/15/74
Cedars (110/177)	~40(~0)	~0(~0)~12[<1]	~20(~3)~2[1.5]	~5000(100)~0[>1]	~110(~0)~1[<1]
Ross Point (105/169)	~40(~0)	164(~10)~14[.7]	10(1)0[>1]	500(~0)~0[0]	240(~0)~1[<1]
Post Falls (102/164)		92(~7)~12[.6]	~0(~0)~8[<1]	~12300(100)0[>1]	50(~0)~0[0]
Harvard Road (92/148)		120(0)57[<1]	~30(~7)~26[.3]	300(0)0	330(~0)~5[<1]
Plantes Ferry Park (84/135)		~64(~0)20[<1]	~10(~2)~8[.3]		310(~4)~2[2]
Upriver Dam (81/130)		112(~0)~11[<1]	~10(~3)6[.5]	~1100(0)~100[<1]	5600(0)~2[<1]
Upriver Drive (77/124)	~140(~0)		~20(~7)~5[1.4]	~2000(0)80[<1]	7600(~8)~1[8]
Gonzaga (74/119)	420(~32)		430(~150)45[3.3]	TNTC(~400)~220[2]	4700(TNTC)TNTC

Table 38. Summary of Bacteriological Data from the Upper Spokane River (11/72-3/74).

Station (RM/K)[1]	No. of Samples	Total Coliform			Fecal Coliform		Fecal Strep.		$R=\frac{FC}{FS}$
		Range	Mean	Median	Range	Mean	Range	Mean	Mean
Cedars (110/177)	12	0-1200	173	31	0-140	13	0- 20	4	3.3
Ross Pt. (105/169)	11	10-5770	1508	240	0-669	106	0-162	45	2.4
Post Falls (102/164)	12	0-9000	1379	475	0-256	69	0-125	26	2.7
Harvard Rd (92/148)	12	0-1800	335	200	0-101	16	0- 98	24	.7
Plantes Ferry (84/135)	4	10-TNTC	128+	187	0- 22	7	2-280	63	.1
Upriver Dam (81/130)	11	0-12600	2113	700	0-170	26	0-TNTC	21+	1.2
Upriver Drive (77/124)	12	10-7800	1768	310	0-164	22	0- 72	17	1.3
Gonzaga (74/119)	11	0-TNTC	1315+	560	0-TNTC	148+	0-TNTC	29+	5.1

[1] RM/K = River Mile/Kilometer

B. Algae Composition

Hynes (1970)[1] in a comprehensive review of the literature concerning the plankton of larger rivers found that diatoms are almost always the dominant algal forms. The most frequently found genera are *Asterionella*, *Tabellaria*, *Fragilaria*, *Melosira*, *Cyclotella* and *Stephanodiscus*. The planktonic green forms are represented by *Scenedesmus*, *Ankistrodesmus* and *Pediastrum*. Certain blue-green algae such as *Anabaena*, *Anacystis* and *Aphanizomenon* occur in warmer waters.

The algae sampled in the Spokane River are within the frequently occurring groups as defined by Hynes and were essentially the same as those enumerated in the 1971-72 sampling period of our earlier study (Funk, Rabe, Filby *et al.*, 1973). Diatoms, as would be expected, dominated the late fall, winter and early spring periods. *Melosira italica* has been the most consistently dominant phytoplankton species at all stations throughout the sampling period. Several species of *Fragilaria* also became prominent in the 1973-74 sampling period--reaching extremely high numbers (89,000 cells/ml in mid-August 1973) at the Upriver Dam station (Figure 73). *Tabellaria sp.* was represented in most plankton samples and reached the highest numbers in mid-October in pool areas of the river. *Cyclotella sp.* and *Asterionella sp.* were present in higher numbers in late spring and also in the colder months. Appendix D contains tabulated plankton data for 1973-74.

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[1] The Ecology of Running Water, Univ. of Toronto Press, Chap. VI, pp. 94-111.

Phytoplankton Productivity

Carbon 14 methods were employed as seasonal checks to estimate the phytoplankton productivity of the river. Of interest was the fact that the most upstream stations, especially the Post Falls pool area, recorded the highest-rate (132 $mgC/m^3/4$ hr) incubation period in mid-October 1973. The next station downstream (Harvard Road) was 21 $mgC/m^3/4$ hr. In fact, during this investigation no downstream station's rate of carbon fixation was greater than 25 $mgC/m^3/4$ hr. Another peak rate of productivity (60 $mgC/m^3/hr$) was measured at the Post Falls station in April 1974 (Table 39). These data favorably compare in time with data taken by Parker (1972) in our earlier study for Lake Coeur d'Alene itself. Peak productivity as measured by Parker utilizing ^{14}C fixation also occurred in the fall (November 1971) at the height of diatom growth. Fixation rates averaged 400 $mgC/m^3/4$ hr--much higher, of course, than those just presented for the river. We would expect this to be the case, since the stabilized condition of a reservoir or lake nearly always results in much higher planktonic production.

Higher phytoplankton productivity in the river may occur in the fall as a result of reduced light, temperature and possibly more nutrients being made available by the fall turnover and destratification of Coeur d'Alene Lake. As previously mentioned in this section, higher bacterial growth was also noted in the upper reaches and may be due in part to nutrient addition of the Coeur d'Alene city treatment plant. This source also would aid in encouraging algae growth. However, even the free-flowing waters of the outlet station at the head of the Spokane River have had consistently higher productivity rates than those measured in the pool areas of Upriver Dam near Spokane. Unfortunately, no ^{14}C

Table 39. Carbon 14 Planktonic Production and Community Structure by Station. 1973-74.

Station / Date	mg C / m^3 / 4 hrs.	Plankton (Total cell count / ml)
Lake Outlet		
October 16	36	Tabellaria, Melosira (811)
April 2	24	Melosira, Asterionella (272)
May 16	11.4	Melosira, Synedra (489)
Ross Point		
October 16	87	Tabellaria, Melosira (747)
April 2	8.4	Melosira, Tabellaria (336)
May 16	26.7	Melosira, Tabellaria (307)
Post Falls		
October 16	132	Tabellaria, Melosira (1550)
April 2	60	Melosira (330)
May 16	20	Melosira, Tabellaria (367)
Harvard Road		
October 16	21	Tabellaria, Melosira (781)
Plantes Ferry		
October 16	24	Tabellaria (448)
Upriver Dam		
October 16	23.4	Tabellaria (268)
April 2	22.8	Melosira (335)
May 16	14.2	Melosira (286)
Upriver Drive		
October 16	18.9	Tabellaria, Melosira (658)
Gonzaga		
October 16	19.5	Tabellaria, Melosira (893)

studies were made during the Fragilaria bloom that occurred at this lower station in August 1973. No doubt, on this occasion, rates at the lower stations would have exceeded those upstream.

It should be noted also at this time that productivity and algal cell counts may not always coincide. Many of the algae counted were most likely recent inhabitants of Coeur d'Alene Lake, and while exhibiting a healthy appearance they may or may not be in an active physiological state (actively engaged in nutrient uptake and cell division). A short-term check on phytoplankton productivity also was made by the chlorophyll "a" method (Chl "a"). Chlorophyll "a" measurements made in mid-October 1973 at the same time as the ^{14}C studies revealed that Chl "a" was 8.04 μg/l at the Post Falls station. This value was 3-4 times greater than for any downstream station with the exception of the Upriver Dam pool area, which was exceeded by only twofold (4.00 μg Chl a/l). Chlorophyll "a" mean measurements are shown by month and station in Table 40.

Periphyton Productivity

Periphyton productivity in a moving body of water usually exceeds phytoplankton productivity several-fold, depending, of course, upon the morphology of the stream bed, the nature of the bottom and the rate at which the water is flowing. Even in deep lakes, periphyton productivity in the littoral communities may exceed that of the phytoplankton by a factor of 5, such as Olson and Odland (1972) have found in Lake Superior.

In terms of overall productivity of the Spokane River, the lower stations, Plantes Ferry to Gonzaga, reverse the trend (downstream stations

Table 40. Chlorophyll "a" and Community Structure by Station, 1973-74.

Station / Date	Mean µg / Chl "a" / ℓ	Plankton Structure
Lake Outlet		
September	--	Gloeocystis, Melosira, Tabellaria, Synedra
October	2.75	Tabellaria, Melosira, Synedra, Fragilaria
November	5.12	Fragilaria, Melosira, Tabellaria
January	3.44	Melosira, Fragilaria, Synedra
February	1.45	Melosira, Fragilaria, Asterionella
Ross Point		
October	2.72	Tabellaria, Melosira, Aphanizomenon
November	2.79	Melosira, Tabellaria, Synedra
January	2.59	Melosira, Asterionella, Tabellaria
February	8.43	Melosira, Asterionella, Synedra
Post Falls		
September	6.07	Tabellaria, Melosira, Synedra
October	8.04	Tabellaria, Melosira, Synedra
November	3.20	Melosira, Tabellaria, Synedra, Aphanizomenon
January	8.43	Melosira
February	--	
Harvard Road		
September	1.24	Tabellaria, Synedra
October	2.20	Melosira, Tabellaria, Synedra
November	2.68	Melosira, Synedra, Fragilaria
January	3.67	Melosira, Tabellaria, Synedra
February	2.32	Melosira, Asterionella, Synedra

Table 40 Continued

Station / Date	Mean µg / Chl "a" / ℓ	Plankton Structure
Plantes Ferry		
October	2.57	Tabellaria
November	3.63	Melosira, Synedra, Tabellaria
January	3.32	Melosira, Synedra, Aphanizomenon
February	1.72	Melosira
Upriver Dam		
September	2.80	Tabellaria, Synedra, Tribonema
October	4.00	Tabellaria, Melosira, Fragilaria
November	2.42	Melosira
January	3.27	Melosira, Asterionella
February	1.72	Melosira, Synedra
Upriver Drive		
September	1.61	Fragilaria, Melosira, Tribonema
October	2.85	Tabellaria, Melosira, Synedra
November	2.21	Melosira, Synedra, Tabellaria
January	2.66	Melosira, Asterionella
February	1.75	Melosira, Fragilaria, Asterionella
Gonzaga		
September	1.80	Melosira, Synedra, Tabellaria
October	2.61	Tabellaria, Melosira
November	3.16	Melosira, Synedra, Tabellaria
January	3.23	Melosira, Asterionella
February	1.94	Melosira, Fragilaria, Asterionella

being more productive). In the spring, summer and early fall periods most of the epipelic and epilithic diatoms (winter population forms) are overgrown by Ulothrix and in some cases Cladophora. Chlorophyll "a" increases from .05 mg/m^2/day to .6 mg/m^2/day. Strands of these filamentous algae exceed 2 cm in length and give areas from the vicinity of Plantes Ferry downstream the appearance of green carpeting under water from July to October. At this time they make up 95-99% of the periphyton biomass. The Plantes Ferry region is especially productive; waters seeping in from the bank areas are considerably higher in nitrates and most likely stimulate the periphyton. Approximately 6% of the winter periphytic population consisted of Ulothrix, Cladophora and Oscillatoria; some Aphanizomenon filaments also were found intermingled with other cells on the slides and rods set out to measure the growth. By late October to mid-November, the slide populations of the downstream stations shift to Tabellaria (45%), Synedra (19%), Melosira (18%), Ulothrix (13%), miscellaneous (5%) very similar to the upstream stations. In the November 1973-January 1974 period, however, there were several exceptions. Large growths of Ulothrix (40-70% of slide populations) occurred at the Gonzaga and Upriver Dam stations. At the same time, Cladophora growth at an upstream station (Ross Point) rivaled the productivity of the lower stations; chlorophyll "a" increased at a rate of .67 mg/m^2/day. Chlorophyll "a" and structure of the periphyton community are shown in Table 41.

It is interesting to note at this time that optimum increases in Chlorophyll "a" occurring in the Spokane River are very similar to regrowth rates (.57 mg Chl a/m^2/day) on rocks stripped of periphyton and allowed to recolonize in the Lake Superior study (Olson and Odlong, 1972). We would expect that, with nutrients constantly passing over the attached algae, greater growth might be expected in a river environment. There are, however, two factors which may mitigate periphyton productivity measurements. In the first instance, the glass slides and rods may not be the most conducive to algal attachment and growth, but are most likely as satisfactory as any artificial substitute (Hynes, 1970). Secondly, there is constant abrasion and washoff by the stream current (which was considerably higher in the studies just completed than in previous years). Very little growth occurred on the slides and rods set out in the early spring of 1974. In fact, much of the equipment was swept away.

Table 41. Periphyton Chlorophyll "a" and Community Structure by Station. 1973-74.

Station / Date	μg Chl "a" / day / m^2	Periphyton Structure (%)
Lake Outlet		
July	43.81	Melosira (76%), Synedra (22%), Misc. (2%)
August	----	
October	13.81	Tabellaria (50%), Melosira (33%), Misc. (17%)
January	----	
February	46.30	Melosira (60%), Synedra (33%), Misc. (7%)
Ross Point		
July	-----	
October	83.0	Navicula (29%), Tabellaria (24%), Melosira (18%)
January	678.0	Cladophora (77%), Melosira (14%), Misc. (9%)
Post Falls		
July	----	
August	----	
October	73.4	Tabellaria (50%), Synedra (18%), Melosira (17%), Misc. (15%)
January	----	
February	6.8	Tabellaria (36%), Synedra (10%), Navicula (26%), Misc. (28%).
Plantes Ferry		
July	607.0	Ulothrix (70%), Melosira (15%), Misc. (15%)
August	632.0	Ulothrix (80%), Melosira (5%), Aphanizomenon (5%), Misc. (10%)
October	631.0	Tabellaria (45%), Synedra (19%), Melosira (18%), Ulothrix (13%), Misc. (5%)
January	42.0	Melosira (76%), Synedra (6%), Misc. (18%)
February	----	

Table 41 Continued

Station / Date	μg Chl "a" / day / m^2	Periphyton Structure (%)
Upriver Dam		
July	421.0	Ulothrix (60%), Oscillatoria (15%), Melosira (15%), Misc. (10%)
August	675.0	Ulothrix (68%), Melosira (20%), Misc.(12%)
October	575.0	Tabellaria (44%), Ulothrix (30%), Misc. (26%)
January	69.0	Ulothrix (40%), Melosira (35%), Misc. (25%)
Gonzaga		
July	----	
August	840.0	Ulothrix (85%), Oscillatoria (10%), Misc. (5%)
October	558.0	Ulothrix (76%), Oscillatoria (15%), Misc. (9%)
January	31.0	Ulothrix (70%), Melosira (18%), Misc. (12%)
February	----	

C. Benthic Macroinvertebrates

Two methods of investigating the macroinvertebrate population of the Spokane River were employed. The first study was made during the period between July 31 and August 9, 1973 and consisted of a comprehensive collection of benthic organisms at four of the seven water quality stations (Ross Point, Harvard Road, Plantes Ferry and Upriver Drive). The second study was a long-term colonization investigation utilizing sampling devices placed in the river for up to six weeks.

Benthic Collection

Samples in this study were collected by a team of two individuals using a modified Hess sampler, Figure 19. The sampler was anchored in .5 to .75 meters of water. The rocks, sediment and materials within the confines of the sampler then were sieved and examined for macroinvertebrates.

The pool area at Ross Point was the only sampling site that was not free-flowing and was not sampled by this means. Bottom samples at this station were attempted through the use of an Eckman grab, but were largely unsuccessful due to the hardpacked nature of the sand bottom. Samples eventually were collected from approximated .09 sq meter (1.0 sq ft) areas by diving. The benthic samples were placed in plastic bags, marked and returned to the lab for separation, enumeration and identification under a dissecting scope.

The invertebrates were identified using Pennak (1953), Usinger (1968) and Mason (1968) and were expressed in numbers per square meter. Macroinvertebrate diversities were expressed using the Shannon function, $D = - \frac{n_i}{N} \log_2 \frac{n_i}{N}$, where n_i is the number of individuals in species

1, 2, 3, etc. and N is the total number of individuals in the sample. Table 42 summarizes the numbers of macroinvertebrates and diversity by station. The organisms are identified in Table D-3, Appendix D.

Table 42. Benthic Collection of Macroinvertebrates from the Spokane River. Sampled from July 31 to August 8, 1973.[1]

Station / Collection Date		Number of Species	Total Number Organisms/m^2	Diversity Index (D)
Ross Point	8/09/73	2	5738	.811
Harvard Road	7/31/73	13	5177	2.406
Plantes Ferry	8/01/73	14	4204	2.08
Upriver Drive	8/01/73	13	1266	2.335

[1] Tabulation by genus is given in Appendix D-3.

The Ross Point station (most upstream river station, Figure 73) yielded two species with a total of 5738 organisms/m^2, giving a diversity index (D) of .811. These results may be somewhat misleading because deviation from standard sampling procedures, as previously described, had to be made because of compacted bottom sediments.

Excellent coverage of the Harvard Road station could be made because of low water levels. Thirteen species made up a total of 5177 organisms/m^2 for D = 2.406. This also may be a diversity maximum because of constantly changing stream depths and velocities. The area is mainly heavy shingle (large boulders) with rock fragments. Simulid larvae were difficult to quantify because of their movement to areas of higher stream velocity.

Plantes Ferry station samples contained 14 species and a total count of 4204 organisms/m^2, giving a D = 2.08. This station also was marked with abundant attached growths of filamentous algae (Ulothrix sp.). Increased numbers and diversity at this station may be related to higher nutrient levels in inflowing waters from the bank areas, as well as from upstream industrial parks.

The fartherest downstream station sampled was Upriver Drive, which yielded a total of 1266 organisms/m^2, with D = 2.335. The rocks in this area had considerable growth on them which consisted mainly of Ulothrix and Cladophora.

A general observation might be made that the dominant species of the upper impounded area (Ross Point) were midge larvae, chiefly Procladius and Glyptotendipes, while the lower free-flowing stations (Harvard--Upriver Drive) were mainly the caddis fly larvae Hydropsyche and the midge larvae Cardiocladius.

Colonization Collection

Macroinvertebrates also were sampled from the Spokane River using a multiple-plate sampler similar in construction to one described by Fullner (1971) and modified from the original sampler devised by Hester and Dendy (1962). The sampler consisted of 14 plates of tempered hardboard, 7.6 cm^2 (3 in^2) in diameter, variably spaced on a threaded rod. A total surface area of .145 m^2 (1.55 ft^2) was available for colonization.

Replicate samplers were attached to a base containing a spike which was driven into the stream bed where shallow conditions existed. They were suspended from stanchions or bridges 1.0 m (3 ft) beneath the surface in the pool areas. The samplers remained in the river for six to eight weeks and were frequently lost as a result of vandalism and the great amount of fluctuations in the river level that occurred during this study. When collected, the samplers were lifted carefully from the water and sealed in large plastic bags. Upon return to the laboratory the plates were removed from the rod and rinsed and scraped to remove attached organisms, which then were counted and identified. Subsamples were counted when large numbers of small organisms were present.

Macroinvertebrates collected from the Spokane River by this method are listed in Tables 43(a), (b) and (c). Values represent the mean of two to three replicates. Seasonal variations in density and composition were apparent at all stations, with greatest density occurring during the fall sampling period, which also coincides with the greater period of primary productivity.

The stations located in the slack-water region behind Post Falls Dam (Outlet, Ross Point and Post Falls) were typified by a large biomass of passive, omnivorous and filter feeders such as Hydra, Simulidae, several species of Chironomidae and oligochaetes. Hydra decreased in numbers downstream--from a maximum abundance of over 24,000 individuals on one sampler at the lake outlet--to less than 30 at Upriver Drive during the fall collection. These coelenterates feed upon zooplankton and are most abundant during times of peak plankton density (Needham and Lloyd, 1937). None are active in the presence of reduced oxygen levels (Pennak, 1953).

The Upriver Dam station located in slack water contained the greatest diversity of organisms (D = 5.96), including the more active caddis fly, mayfly and damselfly nymphs in addition to large numbers of chironomids and oligochaetes. This station was located near the shore in a region of heavy aquatic plant growth (Potamogeton, Ulothrix and Cladophora), which may have provided a more diverse habitat than was present in the open-water stations above.

Table 43(a). Macroinvertebrates Collected by Multiple-plate Sampler from the Spokane River. November 14, 1973.

Taxon	Station				
	Cedars	Ross Point	Post Falls	Upriver Drive	Gonzaga
Trichoptera					
Phryganeidae					
Phryganea sp.				2	
Philopotamidae				4	
Odanata					
Coenagrionidae					
Ischnura sp.		1		6	
Diptera					
Chironomidae					
Orthocladinae	325	800	2155	1013	
Tanypodinae				42	
Hydracarina				1	
Nematodae				3	
Oligochaeta	130	250	135	980	
Mollusca					
Gastropoda					
Physa sp.				5	
Coelenterata					
Hydra sp.	18740	2612	446	29	
Number of Species	31	4	3	10	
Total Number of Organisms/m^2	1995	3662	2736	2085	
Diversity Index (D)	<.5	1.09	.8954	5.96	

Table 43(b). Macroinvertebrates Collected by Multiple-plate Sampler from the Spokane River. February 26, 1974.

Taxon	Station				
	Cedars	Ross Point	Post Falls	Upriver Drive	Gonzaga
Trichoptera					
Hydropsychidae					
Hydropsyche sp.		(Sample Devices Stolen)	(Sample Devices Stolen)	5	(Sample Devices Swept Away)
Cheumatopsyche sp.				9	
Ephemeroptera					
Baetidae					
Centroptilum sp.				1	
Odanata					
Coenagrionidae					
Ischnura sp.				1	
Aeshnidae					
Aeshna sp.				1	
Diptera					
Chironomidae					
Orthocladinae	60			48	
Tanypodinae				1	
Chironominae	2			1	
Simulidae				26	
Hydracarina				4	
Number of Species	2			10	
Total Number of Organisms/m^2	62			97	
Diversity Index (D)	<.5			2.08	

Table 43(c). Macroinvertebrates Collected by Multiple-plate Sampler from the Spokane River. May 22, 1974.

Taxon	Station				
	Cedars	Ross Point	Post Falls	Upriver Drive	Gonzaga
Ephemeroptera					
Baetidae					
Pseudocloeon sp.		(Sample Devices Vandalized)		(Sample Devices Swept Away)	3
Trichoptera					
Hydropsychidae					
Hydropsyche sp.					1
Diptera					
Chironomidae					
Orthocladinae	32		9		155
Chironominae			2		
Simulidae	16		978		4
Hydracarina					7
Number of Species	2		3		5
Total Number of Organisms/m^2	48		989		177
Diversity Index (D)	< .5		< .5		.91

The Gonzaga station was sampled successfully only once in the late spring (May 1974) because of record-high streamflows which constantly abraded the colonization plates and, in some instances, swept the sample equipment away.

Prominent groups of macroinvertebrates and plant materials collected from the Spokane River were prepared in accordance with procedures described in the Methods Section and analyzed for metallic content by atomic absorption and neutron activation methods. The results presented in Tables 44, 45 and 46 indicate that all metals tested for were concentrated in the organisms to levels considerably higher than those present in the river waters.

Table 44. Zinc Content (mg/kg) of Insects and Plant Materials Collected from the Spokane River Utilizing Multiple Plate Samplers.

Date	Plant Materials	Omnivorous detrital-feeders	Omnivorous filter-feeders	
		Chironomidae	*Hydropsyche*	*Simulidae*
2/26/74				
Lake Outlet	2658[1]	971		
Post Falls	2630[2]			1615
Upriver Drive 5/22/74		8696	1013	

[1] Organic detritus
[2] *Stigeoclonium* (a filamentous green alga)

Table 45. Atomic Absorption Analysis of Metals in Organisms of the Upper Spokane River. Collected by Hess and Grab Samplers (Expressed as mg/kg Dry Weight).

LOCATION/ORGANISM	Cu	Fe	Mn	Zn	Cd	Pb	Hg
Ross Point							
Mayflies (*Baetis* *Sp.*)	140	7400	390	3120	70	230	.7
Chironomids (*Glyptotendipes* *Sp.*)	26	2500	240	1050	16	68	.1
Caddisfiles (*Hydropsyche* *Sp.*)	50	6500	920	3060	45	350	.4
Aquatic Worms (Oligochaeta)	17	590	40	450	4.3	16	.3
Aquatic Vegetation (*Elodea* *Sp.*)	81	14500	1400	4200	105	1200	.8
Upriver Dam							
Caddisflies (*Hydropsyche* *Sp.*)	48	619	110	560	29	33	.2
Snails (*Physa* *Sp.*)	340	930	690	1500	131	46	.5
Periphyton (*Cladophora* *Sp.*)	32	2900	450	1900	36	170	1.1
Aquatic Plants (*Potamegeton* *Sp.*)	32	4000	660	1310	20	320	.04
Upriver Drive							
Caddisflies (*Hydropsyche* *Sp.*)	31	2500	550	1660	37	160	1.1
Snails (*Physa* *Sp.*)	250	930	690	1500	131	46	.5
Moss (*Amblystegium* *juratzkanum*)	14	4500	460	1320	8	50	.3

Table: 46. Neutron Activation Analysis of Metals in Organisms of the Upper Spokane River

(Whole Body Analysis except where noted - expressed as mg/kg dry weight)

LOCATION/ORGANISMS	Ce	Se	Hg	Th	Cr	Zr	Cs	Ni	Tb	Sc	Rb	Fe	Zn	Co	Eu	Sb
Plantes Ferry																
Caddisflies																
Hydropsyche Sp.	5.92	1.43	1.067	--	6.67	--	.076	24.0	--	.081	--	456.4	396.	.970	.055	.760
Polycentropus Sp.	2.58	--	.687	.497	13.06	--	.468	--	--	.142	--	657.9	924.6	1.217	.046	1.400
Moss																
Amblystegium juratzkanum	3.0	1.02	.787	.312	18.03	.45	.298	23	.091	.426	16	1328.2	2435	2.023	.100	1.726
Fontinalis Sp.	11.6	1.78	1.221	1.358	52.28	1.78	1.330	--	.169	1.556	18	1294.8	5304	6.716	.346	5.353
Harvard Road																
Caddis flies																
Hydropsyche Sp.	--	--	1.08	.341	7.36	--	.291	72.5	--	.201	--	4395	900	1.66	--	1.465
Polycentropus Sp.	--	--	--	.951	51.98	--	.523	--	--	1.236	--	--	665	2.83	.328	1.939
Moss																
Amblystegium juratzkanum	3.5	1.6	.98	.251	16.0	.30	.325	.25	--	.530	18	1224	2123	2.05	.120	1.65
Aquatic Vegetation																
Equisetem	--	--	--	--	2.14	--	.354	--	--	.028	36	137	485	.152	.016	.154
Upriver Dam																
Caddis flies																
Hydrophsyche Sp.	.392	.19	.147	.07	2.08	--	.04	--	--	.06	3.3	232	561	.443	.01	.910
Polycentropus Sp.	.595	--	.466	--	4.57	--	--	--	--	.03	5.2	194	204	1.31	.03	.218
Snails																
Physa Sp.	2.2	--	.56	.254	5.56	--	.253	--	--	.240	--	932	716.9	.798	.054	.540
Aquatic Vegetation																
Potomegeton Sp.	.90	--	.50	--	5.51	--	.105	--	--	.081	--	321	861	.823	.049	.507
Elodea Sp.	1.71	--	.753	.209	16.46	--	.124	--	--	.177	--	721	1863	1.450	.065	1.058
*Potomegeton Sp.																
Leaves	3.38	--	2.04	.162	8.614	--	.190	--	--	.199	20.5	11.29	2298	.926	.050	.468
Stems	1.3	--	--	.221	8.708	--	.321	--	--	.261	--	747	246	.630	.043	--
Roots	13.21	3.09	3.02	1.233	18.044	--	1.843	--	--	2.081	156.8	9728	4041	4.589	.470	6.85

* Portion of plants analyzed separately.

D. Analysis of Sediment Samples

Fifteen cores were attempted by coring barge at several of the water quality stations in the Spokane River. No attempts were made at Harvard Road, Plantes Ferry, Upriver Drive or Gonzaga stations because of shallow conditions and rapidly moving water. Only one core was retrieved successfully by coring barge; this 5cm core was taken at the Ross Point station. The river bottom, almost without exception, is well scoured to heavy shingle, boulders or basalt bedrock. The sediment taken for testing from the other stations was recovered by hand-driven cores, Ekman grab or diving.

It was our conclusion that the existing sediment deposits most likely are shifted and mixed almost yearly. No stratified sediments were found. The results of the sediment analyses are shown in Table 47. The fact that much of the sediment appears to be shifted at least once a year probably precludes the development of stabilized invertebrate colonies along the river (except for a few quiescent pockets). This may help to explain a slightly lower diversity index than we expected. The movement of sediment down the river in mid-January and February abraded and scoured nearly all growth off our periphyton slide and tube equipment. The sediment and rapidly moving waters also removed the invertebrates from the colonization sampler and, in many cases, the sampling equipment as well.

E. Analysis of Tree-Ring Structure as an Indicator of Metal Uptake along the Spokane River.

A short-term intensive study was made in the Upper Spokane River to determine if large vascular plants such as trees growing in the proximity

Table 47. Atomic Absorption Analysis of Sediments Taken from the Spokane River, August, 1973. (S = Sediment Surface.)

Station / Depth		Element (mg/kg)							
		Zn	Mn	Cu	Cr	Ni	Pb	Cd	Mg
Lake Outlet	S-2cm	1120	474	26.9	32	16.38	286	6	2436
Ross Point[1]	S-1cm	3700	1388	24.2	51	22.5	840	9.6	2274
	2-4cm	2780	682	18	31.4	16.4	340	17	3600
Post Falls	S-1cm	--	1478	36.4	63.2	25.9	1080	44.2	3826
	2-4cm	1424	342	17.8	44	22.6	132.8	Tr	3320
	4-6cm	64	396	22.4	62	30.6	---	--	3734
Harvard Road	S-1cm	1700	890	22.8	54.8	26	300	8.6	4940
Plantes Ferry	S-1cm	82	310	24.6	66.6	36.8	---	--	3760
	2-4cm	62	307	22	56.8	27.9	---	--	
Upriver Dam[2]	S-1cm	4910	437	24.2	42.8	23.8	98	3	3920
	2-4 cm	278	100	14	24.2	16.38	---	Tr	1540
Gonzaga	S-2cm	190	380	18	33.8	20.8	---	1.6	3010

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[1] Only sample successfully taken by coring barge.

[2] Hand driven in 1.0 meter of water; all other samples taken by dredge or diving.

of the river could concentrate metals as did the algae and aquatic macrophytes tested in our previous OWRR study (Funk, Rabe, Filby et al., 1973). The literature and preliminary work cited in the following paragraphs have shown that metallic concentration takes place, but more importantly there is strong evidence that trees may not only act as detectors of metallic pollution but may actually "sense" variations in metallic loads in rivers which then can be related to time.

Warren and co-investigators (Warren, 1972; Warren, Delavault and Cross, 1966; Warren, Delavault and Barasko, 1968) have shown that leaves and materials taken from trees grown in the vicinity of ore deposits contain orders of magnitude more As, Cu and Zn than those grown in less mineralized areas and have demonstrated that Douglas-fir concentrates As by a factor of between 10-100 greater than most other trees and plants. These observations demonstrate that trees are sensitive indicators of dissolved metal ion concentrations in soils. Ellis (1962) determined the mineral content of the Grand fir grown east and west of the Cascade Mountains and observed higher Mo, Zn, Ag, Pb and Sr concentrations for trees grown in several drainage areas of the highly mineralized area of northeastern Washington and northern Idaho and observed that trees abnormally high in Na grew near salt water. Holtzman (1970) determined the ^{210}Pb content in black oak, white oak and hickory and demonstrated that the ^{210}Pb concentration decreased exponentially as a function of growth-ring age. Holtzman's data also suggest that translocation, while not zero, is small enough that variations of lead concentrations may reflect environmental factors. We found no data in the literature supporting the assumption that metal ions are incorporated into growth rings via leaves and needles and therefore feel at this time that air pollution as a direct path for the introduction of metals into growth rings of trees has yet to be established. However, as previously mentioned, the research cited suggests the possibility of monitoring long-term heavy metal concentrations in streams by determining the heavy metal content of growth rings of trees growing on river banks.

Rivers flowing through the active Coeur d'Alene mining region of northern Idaho provided a good test of this hypothesis because mining and smelting effluents have polluted the Coeur d'Alene-Spokane River system for the past 70+ years (Figure 1). In addition, mining activities for this region are well documented (Reid, 1961). Furthermore, as mentioned in the Introductory Section, water quality parameters of the Spokane River and Coeur d'Alene Lake have been objects of intense research (Mink, Williams and Wallace, 1971; Funk, Rabe, Filby *et al*. 1973; Savage and Rabe, 1973). Of particular importance was the fact that we determined the metals distribution to be a function of sediment depth in Coeur d'Alene Lake in our earlier study (Funk, Rabe, Filby *et al*. 1973). The sediment and mining activity data then provide comparative bases to establish if the metal content in rings of trees growing along polluted streams can be used to record water quality data over long periods of time. With these factors in mind, we attempted to use three pine trees growing on the banks of the Spokane River as sensors of the river's metal ion concentrations for the past 60 to 70 years.

Cores were taken from ponderosa pine trees (*Pinus ponderosa*) growing on the banks of the Spokane River at Post Falls and Ross Point, Idaho to determine if metal concentrations in the tree rings of these trees varied significantly. The Post Falls ponderosa pine was a healthy 41-

year-old tree growing about three meters from the high-water level of the Spokane River. The Ross Point ponderosa pine growing on the bank edge (high-water level) was dying and was older than 64 years. Since the cores from these trees were perpendicular to the tree rings, the concentrations for each section of the cores were averaged over the rings sampled. Individual growth rings of these trees could not be used because sample sizes were too small for the precise determination of their metal content. A third ponderosa pine, about 57 years old, growing at Corbin Park, and with a large root in the Spokane River, was cut down and a section was removed for analysis. To obtain more refined data, cores parallel to the tree rings were taken from the Corbin Park tree at five-ring intervals. The Corbin Park tree was considered a "better" sensor than the Post Falls and Ross Point trees because of the larger samples used, considerably better counting statistics, the shorter time intervals sampled and, most importantly, the fact that this tree had a large root in direct contact with the Spokane River.

Data for the Post Falls and Ross Point trees were combined to give the metal ion concentrations of these trees for the past 64 years, averaged over six- to ten-year intervals. This was done because the outer Ross Point core, which comprised the dying portion of the tree, covered a 40-year interval--between 1931 and 1972--and did not yield information about fluctuations of metal concentrations. The average metal concentrations in the two trees were in reasonable agreement (30 percent) but the Fe and Zn concentrations in the Ross Point tree were three to five times higher than in the Post Falls tree. The fact that Fe and Zn concentrations are quite different cannot be explained readily and serves to emphasize the fact that soil conditions, the tree's health, contact with the river and possibly other factors may influence metal uptake by the tree.

Silver, Zn, Co and Fe were observed in all three trees but only the Corbin Park data are included, for the reasons mentioned above. The Na, K, Mn, La, Sb and Au data are included mainly to give an idea of their concentrations in ponderosa pine trees and for comparison to other data (Ellis, 1962). These elements were not observed in the Corbin Park tree samples because they were counted after decay times sufficient to allow the short-lived radionuclides to decay away. This was done because Zn, Co, Fe, etc. were considered to be better indicators of stream pollution and because of the high concentration (400 μg/ml) of Zn observed in the Spokane River.

Table 48 indicates the amount of metal concentrations found in the growth rings of the Post Falls, Ross Point and Corbin Park trees. Examination of these data indicate metal concentration fluctuations, some significant at the 95% confidence level. To determine if these fluctuations could be related to environmental disturbances in the Coeur d'Alene mining district near Wallace and Kellogg, Idaho (about 64 km from the sampling points), the data were compared to the tons of ore mined annually in this region (Reid, 1961). Examination of the mining data, shown in Figure 79, revealed maxima at 1918, 1928 and 1948 and minima at 1922, 1932 and 1954-57. The 1922 and 1932 dates represent economic depressions.

The Coeur d'Alene Lake sediment core data obtained in our earlier study (Funk, Rabe, Filby et al. 1973) also were compared to the tree-ring data. The sediment core used for this comparison was taken 1.6 km from the mouth of the Coeur d'Alene River and was chosen because the

Table 48. Metal Concentrations in mg/kg of Dry Wood for Ponderosa Pine Trees Growing on the Banks of the Spokane River, Idaho

Date Rings Formed	Na	K	Mn	La	Sb	Au	Hg	Cr	Ag	Rb	Zn	Co	Fe	
	Ross Point						Corbin Park							
1908-14	31.3	652	1.55	0.0044	0.0049	0.0017	-	-	-	-	-	-	-	
1916-18	32.0	676	1.54	0.0053	--	0.0010	0.10	.10	.02	.17	100.2	.067	16.5	
1918-21							.011	.10	.09	.21	92.6	.053	14.8	
1925-27	108.8	631	1.21	0.0147	0.0029	0.0011	.005	.90	.14	.08	73.3	.049	12.3	
1930-32							.010	.10	.22	.06	107.2	.051	14.0	
	Post Falls													
1935-36	36.0	1381	1.32	0.0029	0.0028	0.0024	<.007	.58	.12	.73	90.2	.064	17.2	
1939-41	116.8	1588	0.97	0.0082	0.0028	0.0024	<.007	.15	.06	.48	109.3	.046	11.3	
1944-46							.017	.09	.15	.77	97.3	.019	5.2	
1949-51	117.0	3311	1.63	0.0015	0.011	0.0031	.019	.09	.15	.92	86.2	.026	11.3	
1954-56	71.0	3034	1.41	0.0049	0.0024	0.0011	.019	.36	.09	.67	78.3	.050	10.7	
1958-61							.020	.09	.18	.69	62.2	.033	8.5	
1965-66	143	2847	1.55	0.0051	0.0051	0.0035	.016	.14	.09	.80	41.0	.026	52.2	
1967-71							.022	.10	.05	.47	37.7	.030	7.0	
	.5	39	.04	.0005	.0002	.0002	.003	.02	.01	.08	.4	.007	0.5	(a)
	1.4	110	0.11	0.0014	.0006	.0006	.009	.06	.03	.23	1.1	.019	1.4	(b)

(a) These are the average standard deviations for each metal concentration, based only on counting data.
(b) A significant difference is defined as $/C(1) - C(2)/ \geq 2.0 \sqrt{2 \sigma_{ave}}$.

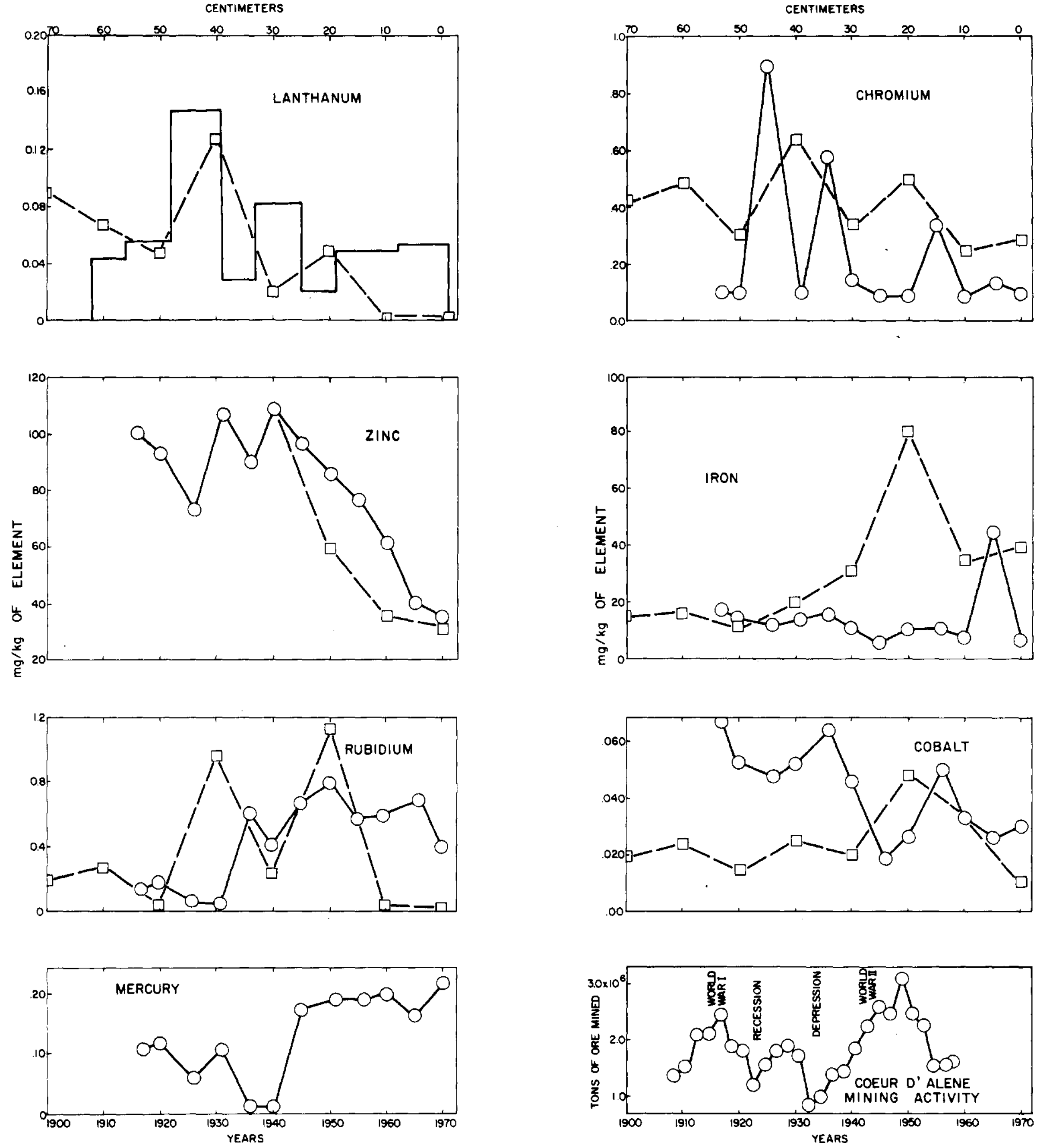

Figure 79. Tree and Sediment Core Data in Relation to Mining Activity. (The solid lines represent mg of metal per kg of dry wood for the Corbin Park ponderosa pine tree and the dashed lines are mg of metal per kg of dry Coeur d'Alene Lake sediment. Post Falls and Ross Point La data are used in the upper left corner of the figure. The historic mining data are shown in the lower right corner of the figure.)

sediment would be disturbed minimally by river scouring action. These data represent an even more coarse-grained approach to the detection of metal ion concentrations in the Coeur d'Alene River, but the problem of holdup in Coeur d'Alene Lake is eliminated. The sediment, tree-ring and mining data are shown in Figure 79.

The Fe data for the Corbin Park and Post Falls trees showed one prominent, recent maximum. If these data are displaced about 15 years, they are in agreement with the one major peak observed at a sediment depth of 20 cm and the post-World War II mining activity maximum. It should be noted that the Fe concentration for the 1962-1972 period of the Post Falls tree was 62.7 μg/g, compared to the peak value of 52.2 μg/g for the Corbin Park tree. Both the tree and sediment data indicate a major Fe peak reflecting the mining activity shortly after World War II.

When the Cr data for the Corbin Park tree are displaced about nine years, they are in rough agreement with the mining activity in the Coeur d'Alene sediment core data. The sediment core data lag the mining two to three years for the 1948 and 1928 mining activity peaks, but the 1917 mining peak follows the core peak by about five years.

On the basis of the $2.0 \sqrt{2 \quad _{\mathrm{ave}}}$ criterion, it is difficult to correlate the Co data with the mining or sediment core data. There is a minimum that corresponds to the 1944-1951 period and it possibly is related to the 1932-1940 depression.

With the exception of the 1953-1955 minimum, the Zn data for the Corbin Park tree correlate with mining activity. The Zn concentration in the Corbin Park tree decreases at about the same rate as the sediment but with a five-to ten-year delay. The recent decrease in Zn^{2+} concentration in the tree and sediment may be indicative of more efficient Zn recoveries or decreased production at the upstream mines and smelters (or both).

Mercury concentrations in the Corbin Park tree increase with time, and a minimum is observed which corresponds to the 1932-1940 depression.

The Na, K and Rb concentrations in the Corbin Park, Post Falls and Ross Point trees increased significantly about 30 to 40 years ago. These data cannot be shifted to fit either the mining or the sediment data and suggest that other contributions, such as timber harvesting, sewage disposal, etc., probably account for the increase. The data are consistent with Ellis's (1962) observation that trees growing near salt water have high Na concentrations.

The combined Mn data for the Post Falls and Ross Point trees roughly correlate with the mining data but do not agree with the sediment core data, which showed a recent maximum similar to Fe. Since the Mn data represent six- to ten-ring (year) averages, some maxima could be averaged out. These data emphasize the advantages of sampling individual rings.

Except for the World War I peak, the Ag data follow the mining data by about four years. Antimony concentrations in the Post Falls-Ross Point composite also follow the mining data. With the exception of the pre-1932 maximum, gold also follows the mining data. The Sb and Au data are averages and composites should be considered in the same category as Mn--that is, with reserve. The La data for the Post Falls-Ross Point composite show one large maximum, which agrees with the sediment core data, and indicate that a large La pulse passed through Coeur d'Alene Lake between 1920 and 1930. A smaller La pulse may have passed through in the 1940's.

The La and Fe data, shown in Figure 79, can be used with our sediment core data to obtain a rough estimate of the recent sediment deposition rate for the Coeur d'Alene Lake delta region. These data indicate that the sediment deposition rate has been 1.0 cm/yr and are indicative of the fact that mining activity in the Coeur d'Alene region was fairly constant for the 1908-1957 period. Since the Coeur d'Alene Lake cores were about 80 cm long, approximately 80 years of mining and other environmentally significant human activities have taken place in the Coeur d'Alene region. It is noteworthy that mining operations started in the Coeur d'Alene region in 1888 (Flaherty, 1972).

These experiments are admittedly preliminary in nature, but they suggest that long-lived trees growing in intimate contact with rivers may be used to monitor variations of metal ion concentrations in rivers for times approaching a century. If allowances for holdup in Coeur d'Alene Lake are made, some of the metal concentrations correlated with the mining activity data. The research described here is analogous to attempts to correlate the ^{14}C content of tree rings with historic sunspot data (Baxter and Farmer, 1973), which is basically a signal-to-noise problem (Damon, Long and Wallick, 1973). Just as the sunspot correlation needs to be treated with reserve, so should the data reported here. Obviously, more research will be necessary to establish the value of this method of monitoring metal concentrations of rivers. For example, the average yearly flow of the Spokane River was not considered in the analysis of the data. Another factor not considered was the background or precultural levels of these metals in the trees. These data can be obtained if longer-lived trees are sampled. The location of the tree should be chosen carefully to eliminate holdup in lakes. Future research should include these factors. If a 100-year-old tree growing in the Coeur d'Alene River were located and tested, the time lag caused by holdup in Coeur d'Alene Lake would be eliminated and, if river flow rates and background levels are included, regression analysis could be used to determine the extent of correlation between existing metal concentrations in the trees and the river water metal concentrations. Future experiments are planned to test this hypothesis.

F. Analyses of Fish in the Spokane River and Upper Coeur d'Alene Drainage

Fish from the Spokane River were collected by gill nets at Harvard Road and Upriver Dam in August of 1973. They were brought to the Environmental Engineering laboratories on ice and frozen until dissection. Fish from the upper Coeur d'Alene River drainage were collected (by electroshocking) by personnel from the U.S. Bureau of Sport Fisheries and were frozen or preserved in formalin.

All fish tested were dissected with acid-cleaned stainless steel scissors, scapels and plastic-coated forceps. Tissue for neutron activation analysis was placed in acid-cleaned two-dram polyethelene vials and freeze-dried. The vials were capped, heat-sealed and irradiated at the WSU Nuclear Radiation Center in the Triga III reactor. A germanium-lithium detector (47cc) was used to detect gamma peaks, which were recorded on magnetic tape. Peak areas were calculated on an IBM 360/67 computer. Details of the activation procedures are given in the Methods Section (Filby, 1970, and Shah, 1970a, 1970b).

Tissue for atomic absorption analysis was placed in acid-cleaned flasks, oven-dried at 105 C and digested with distilled perchloric and nitric acids (Leonard, 1972). The sample was filtered through acid with sintered glass filters and brought to 10- or 25ml volume. The samples then were analyzed on a Perkin-Elmer 303 atomic absorption spectrophotometer using a flame technique or high-temperature graphite absorption. Muscle and liver tissues usually were analyzed by both neutron activation and atomic absorption. Other smaller tissues for each fish were analyzed by either neutron activation or atomic absorption.

Iron, Zn and Cr were analyzed by neutron activation and atomic absorption. The comparisons for Fe and Zn are given in Figures 80 and 81. Absorption analysis of Cr is not sensitive enough to accurately detect concentrations below one to two mg/kg when small sample weights are used.

For both Fe and Zn the slopes of the lines are close to one, but the y intercepts are considerably greater than 0. The large y intercept may be due to the greater sensitivity of the activation analysis, or some metals may be volatilized by the 105 C drying used in the atomic absorption preparation. The great difference in the Fe analysis probably is due to nonhomogenous samples. Iron is a constituent of the blood, and the greatest divergence among the two methods occurs in tissue such as the heart and liver, which contain relatively large amounts of blood. Iron is a relatively innocous metal and is toxic only at high concentrations. It is included here only for a comparison of methods.

Game species collected from the Spokane River were brook trout (*Salvelinus fontinalis*) and rainbow trout (*Salmo gairdneri*). The rainbow trout were collected mainly from the Harvard Road site, and brook and rainbow were collected at the Upriver Dam station. The trout collected from the upper Coeur d'Alene drainage were cutthroat (*Salmo clarki lewisi*) and had a mean weight of 61 grams compared to 199 grams for the Spokane River fishes.

We tested the two station collections of Spokane River fishes for differences in Zn concentration and found no significant difference. We tested brook trout against rainbow and found no significant difference. The Spokane River fishes were grouped into two weight classes of 0-100 grams and 100+ grams, and no significant difference was found. Zinc

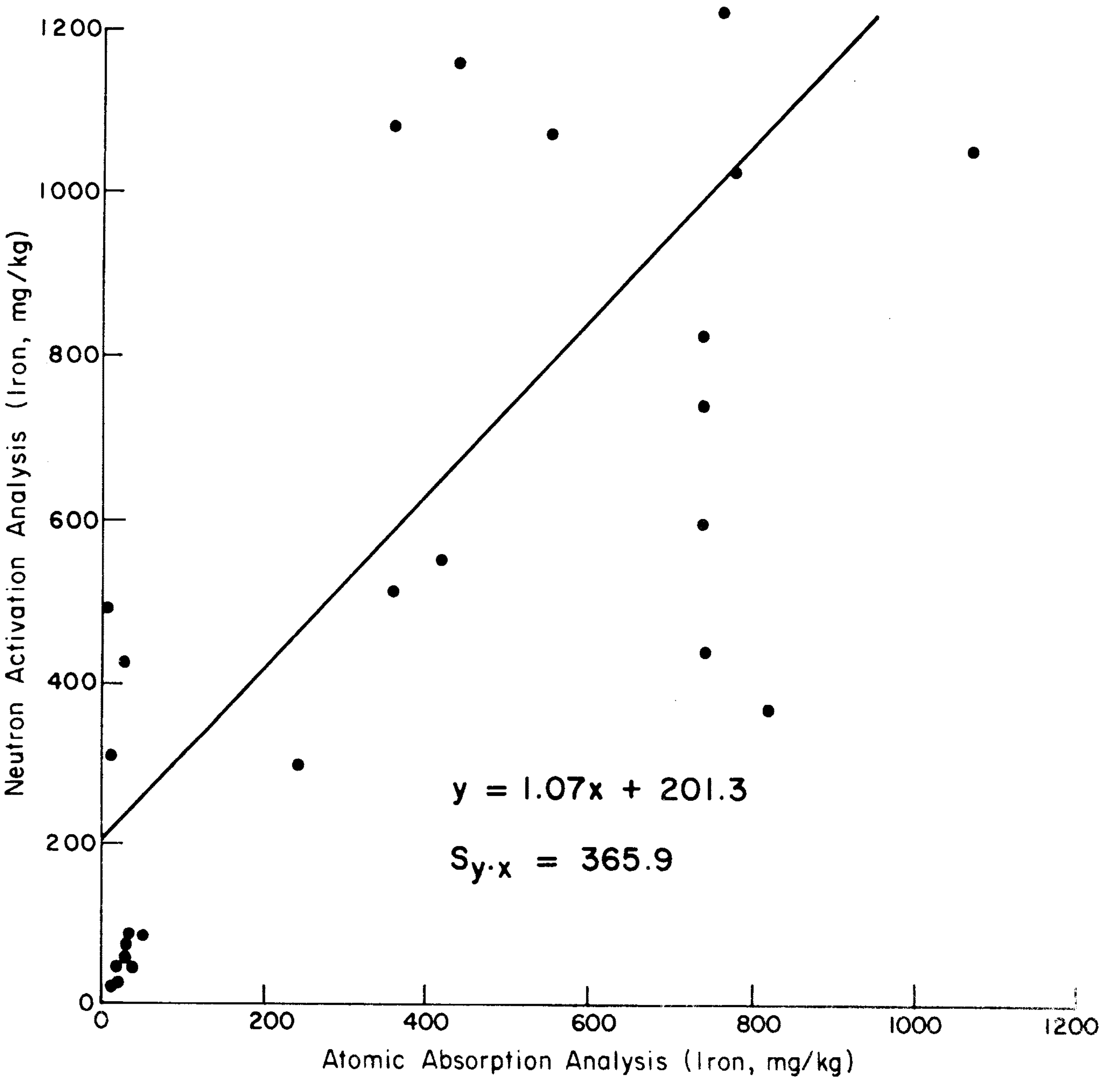

Figure 80. Comparison of Neutron Activation and Atomic Absorption Analyses for Measurement of Iron in Fish Tissues.

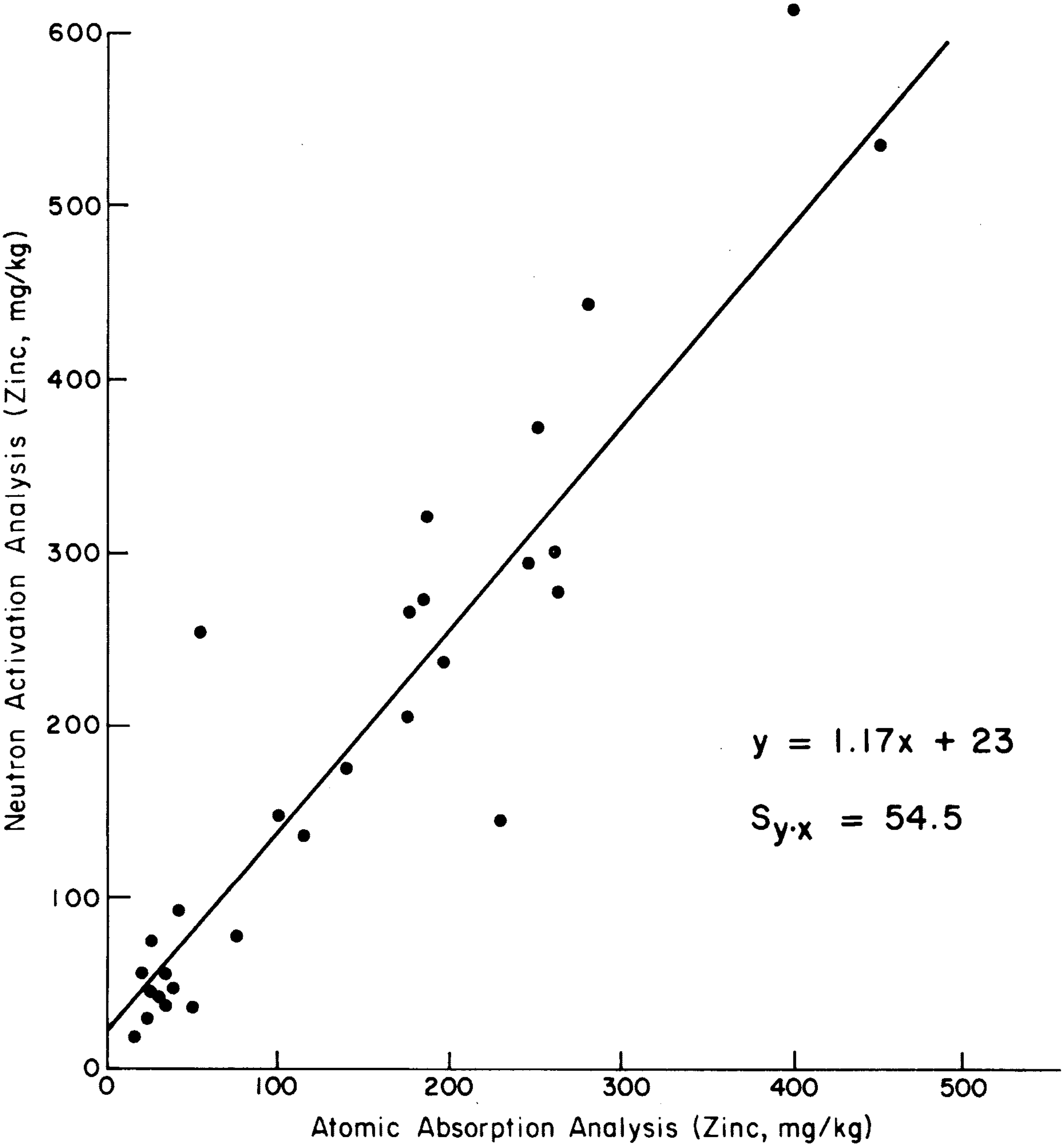

Figure 81. Comparison of Neutron Activation and Atomic Absorption Analyses for Measurement of Zinc in Fish Tissues.

concentrations in the liver and muscle of trout from the upper Coeur d'Alene drainage were significantly lower at the 95% confidence level than in liver and muscle tissue of Spokane River fishes (Figure 82). Copper and Cd were also significantly higher in liver tissue of trout from the Spokane River, but there was no significant difference in concentrations in muscle tissue of these two groups of fishes (Figure 83, and 84). These data suggest that fishes in the Spokane River are not excreting Zn fast enough to keep down muscle concentrations, while Cd and Cu are being excreted fast enough to keep muscle concentrations at normal levels.

We did not find in the Spokane River fishes the inverse correlation of metal content with size (Figure 85) that other researchers have found (Hannery, 1966). We did find a significant inverse correlation in the upper Coeur d'Alene trout (Figure 86).

Eight different organs from the Spokane River fishes were tested for metal concentrations (Figure 87). Organs with large amounts of blood, such as the heart, kidney and spleen, and organs with enzymatic activity, such as the liver and pyloric caeca, contained the highest concentrations of heavy metals. Muscle and brain tissues for the most part contained the lowest concentrations. This pattern of concentration shown for Zn in Figure 87 was similar for Co, Cd, Cu, Mn and Se. All of these metals except Cd have known enzymatic functions (Bowen, 1966).

When Sb and Cs were in concentrations large enough to be measured accurately, they showed little variation (7-50%) among different tissues in the Spokane River fishes. In the fishes from the upper Coeur d'Alene drainage, concentrations of Sb, Eu, Sc and Th were higher in liver tissue than in muscle tissue. Only Cs did not show variation among tissues in these fishes.

There is a paucity of methods described in the literature which can be compared directly to those we utilized.

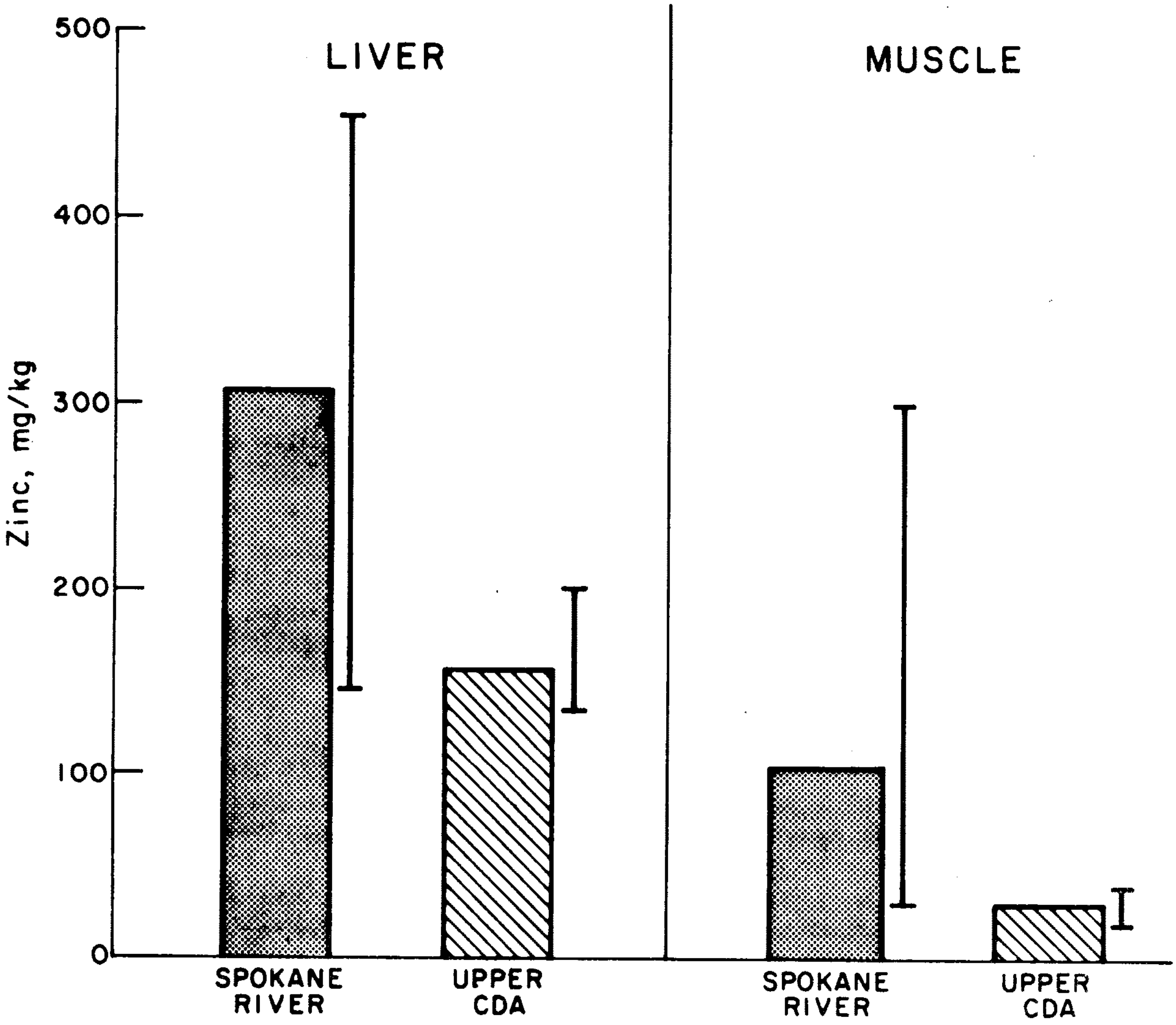

Figure 82. Comparison of Zinc in Liver and Muscle Tissues of Fishes from the Upper Coeur d'Alene and Spokane Rivers (Line to Right of Figure Represents Range of Measurements).

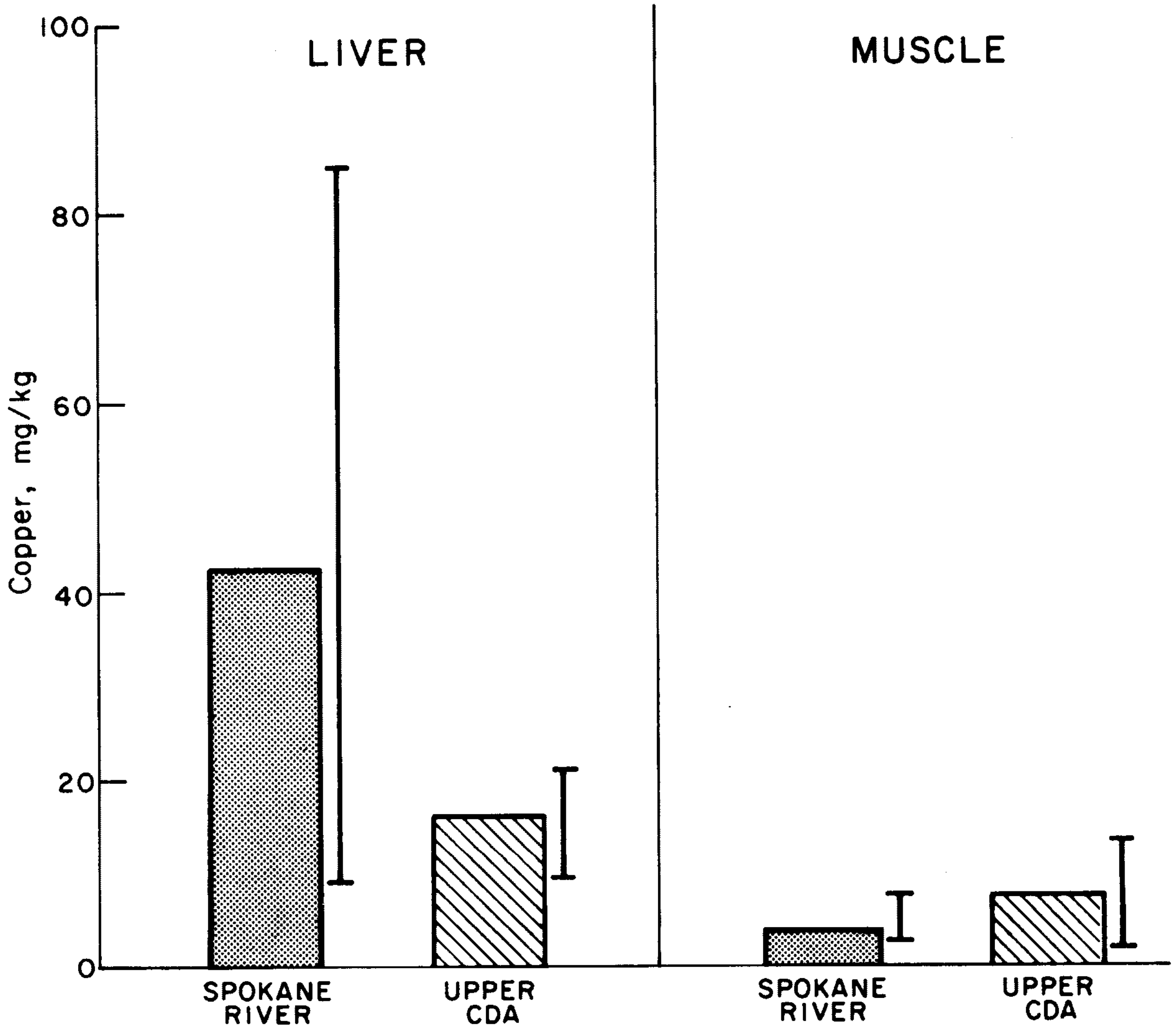

Figure 83. Comparison of Copper in Liver and Muscle Tissues of Fishes from the Upper Coeur d'Alene and Spokane Rivers (Line to Right of each Figure Represents Range of Measurement).

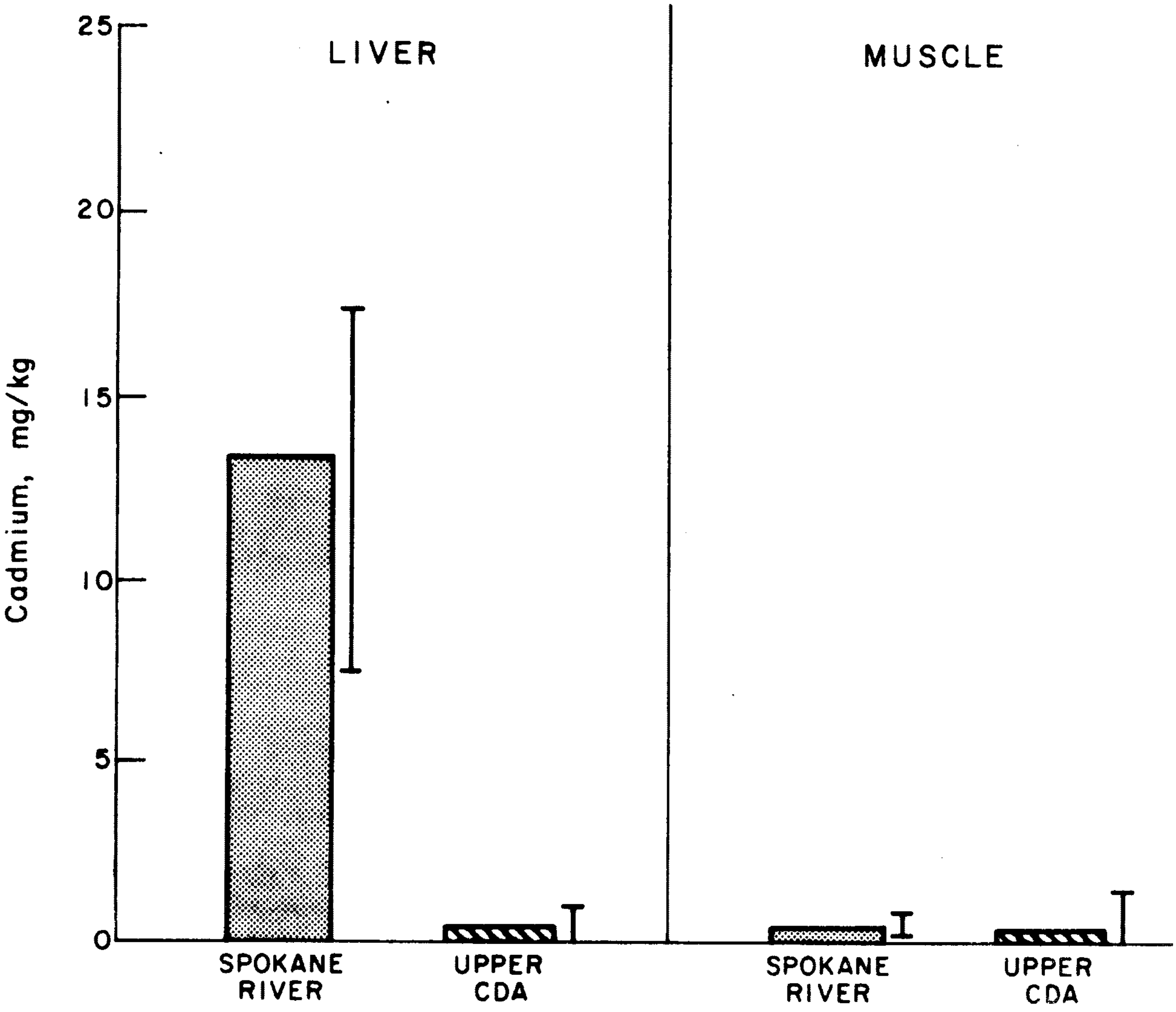

Figure 84. Comparison of Cadmium in Liver and Muscle Tissues of Fishes from the Upper Coeur d'Alene and Spokane Rivers. (Line to Right of each Figure Represents Range of Measurements).

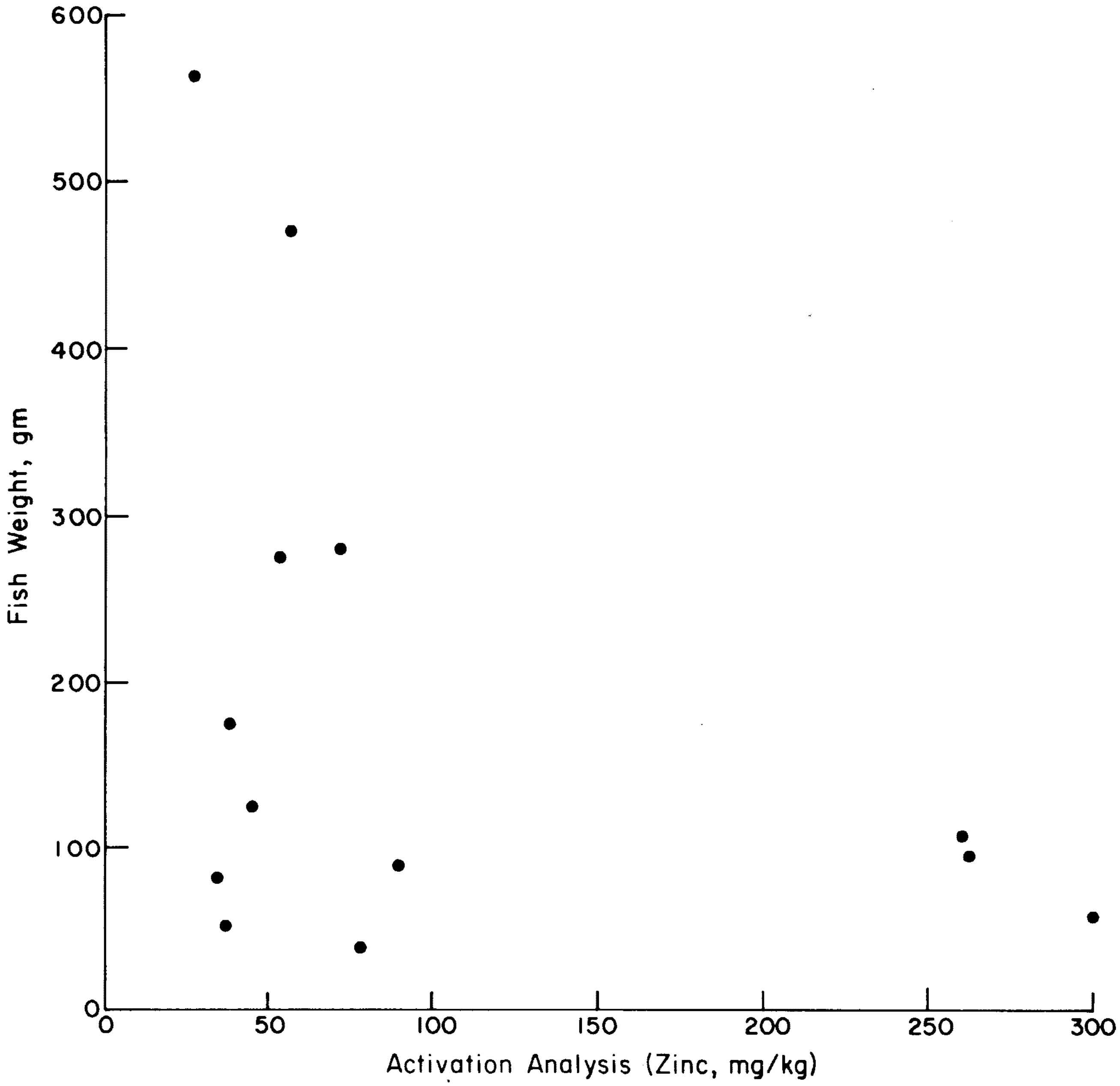

Figure 85. Comparison of Weight and Metal Content of Fishes from the Spokane River.

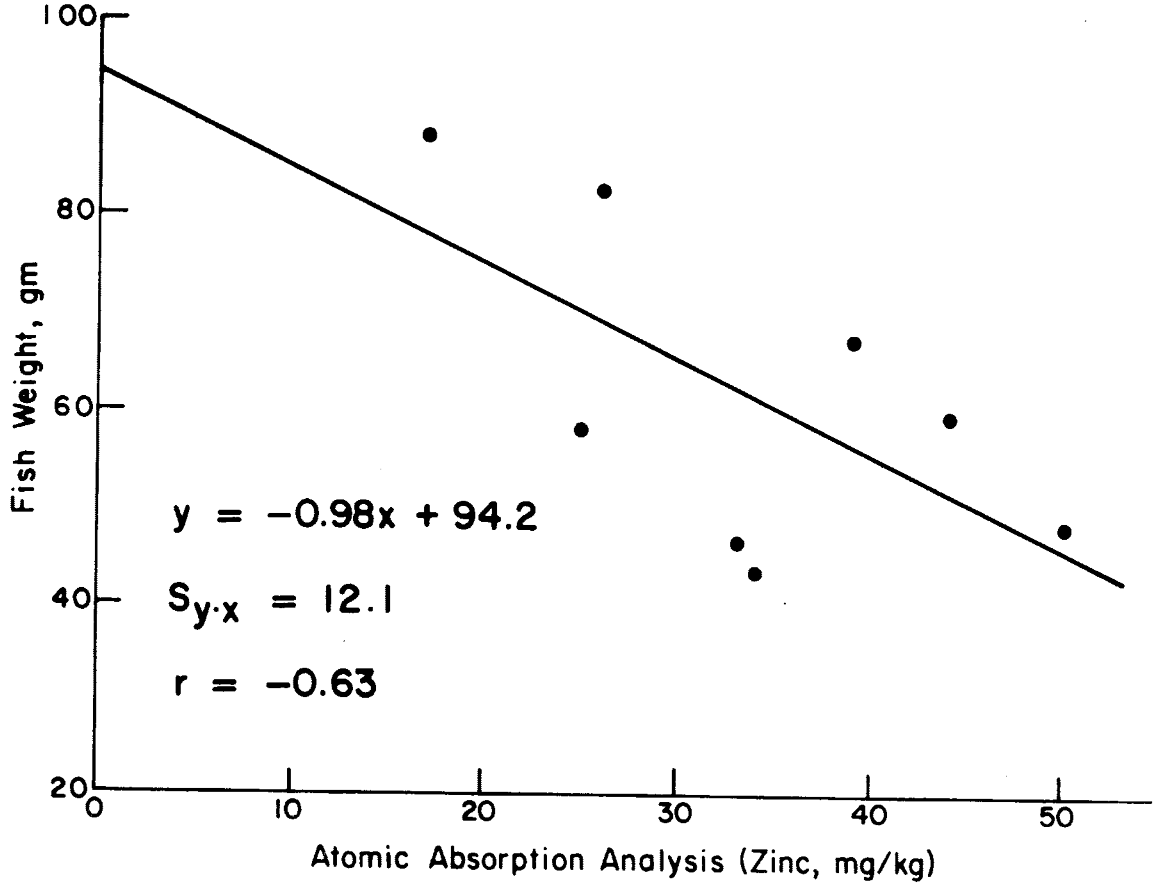

Figure 86. Comparison of Weight and Metal Content of Fishes from the Upper Coeur d'Alene River Drainage.

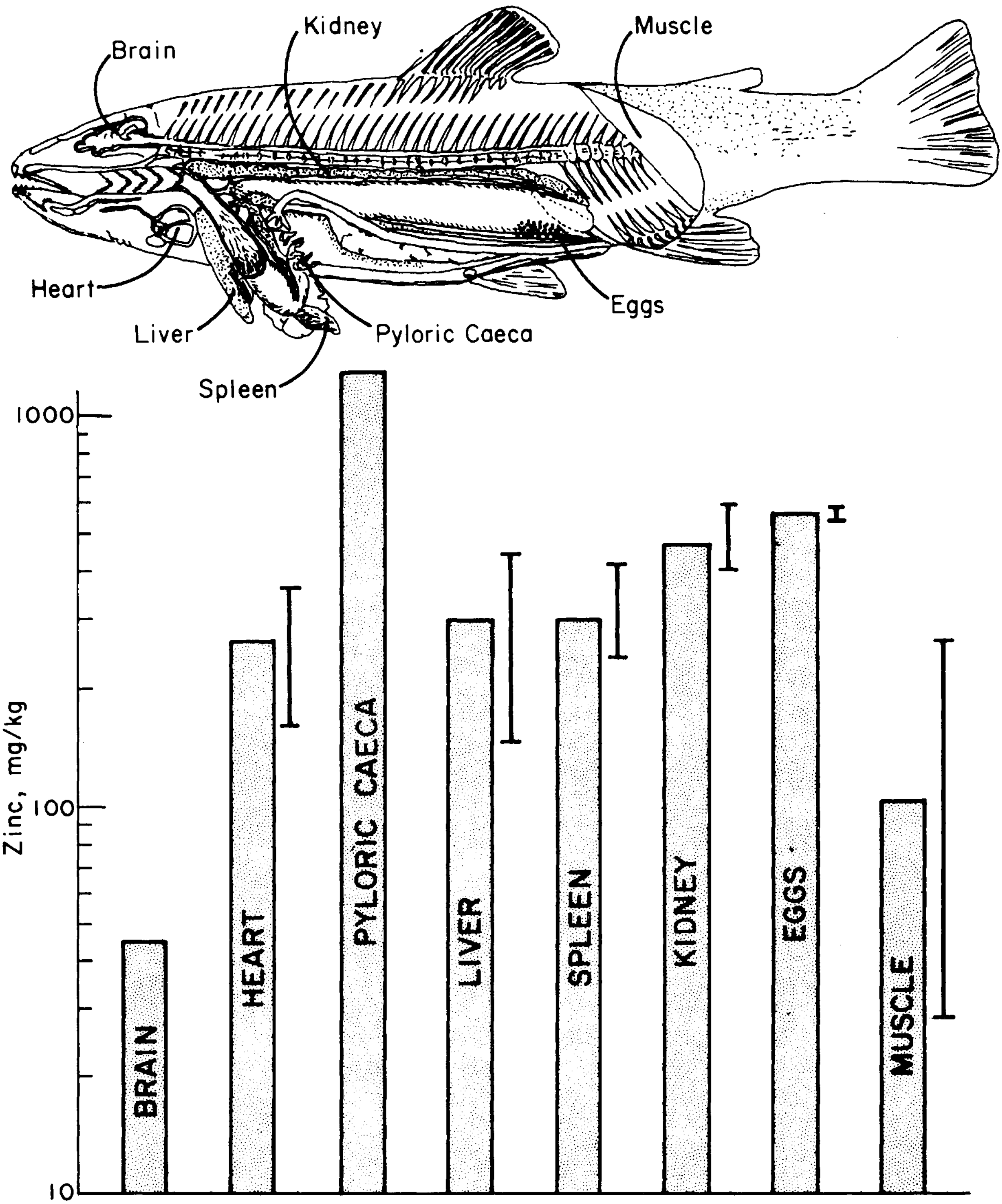

Figure 87. Zinc Concentration in Various Organs of Fishes from the Spokane River.

G. Spokane River Study Summary

The condition of the upper Spokane River as measured by usual environmental engineering water quality criteria such as dissolved oxygen, biochemical oxygen demand, temperature and nutrients would be classified as good. For the most part the bacterial classification at the upper four stations would meet Washington State Class A standards, and the lower four stations Class B standards. Extensive limnological and benthic studies indicate that the overall productivity of the upper four stations is directly controlled by the water quality of Coeur d'Alene Lake, while that of the lower four is controlled in main by the lake but also by nutrient addition and waste discharge to the river as it courses the valley toward the city of Spokane. Statistical analyses have confirmed this phenomenon, especially in the case of the addition of nitrate-nitrogen.

There is a considerable concentration of various metallic elements to very high levels in the algae, periphyton, aquatic macrophytes and trees in and adjacent to the river. The benthic invertebrates that feed upon algae and detrital materials also have high levels of these metals in their tissues (Tables 44, 45, 46). Salmonid fishes that inhabit the Spokane River feed to a large extent upon the benthic insects and in so doing receive considerable amounts of metals. It appears, however, that there is a significant reduction in the amounts of metals retained in animal tissues as one progresses up the food chain.

There may be subtle effects such as viability of fish eggs or survival of the offspring that are not readily apparent and should be investigated extensively.

The algae and periphyton do not appear to be affected, since the presence and growth of species in the river correspond to other rivers in the area and to those described by Hynes (1970) as inhabiting rivers and streams, with the possible exception of certain sensitive species such as Selenastrum capricornutum. The main controlling factors in the Spokane River appear to be streamflow, substrate nutrients and temperature.

With the exception of the Ross Point station, the macroinvertebrate populations appear to be affected more by the shifting and abrading action of the stream (loss of substrata and food sources as a result of changes in streamflow) than by the effects of metal poisoning. It is felt, however, that comprehensive efforts should be made to reduce both the metallic and nutrient inflow into Coeur d'Alene Lake. If this body of water becomes eutrophic, with attendant loss of dissolved oxygen and reduced pH in the hypolimnion, the release of soluble metallic elements (from the extensive deposits now occupying the lake bottom) could exert a far greater effect upon the macroinvertebrate and fish life of the upper Spokane River.

The results of research conducted by Van Meter (1974) on the Clark Fork River in Montana are compared with our data in Figure 88. Van Meter's data were reported by wet weight and have been converted to an approximate dry-weight basis by multiplying by 5. His data fall between our values for Zn and Cd and are greater for Cu. Van Meter utilized a closed-vessel digesting technique, which may indicate that some of the variations we find between our atomic absorption and neutron activation results may be due to the digestion procedures.

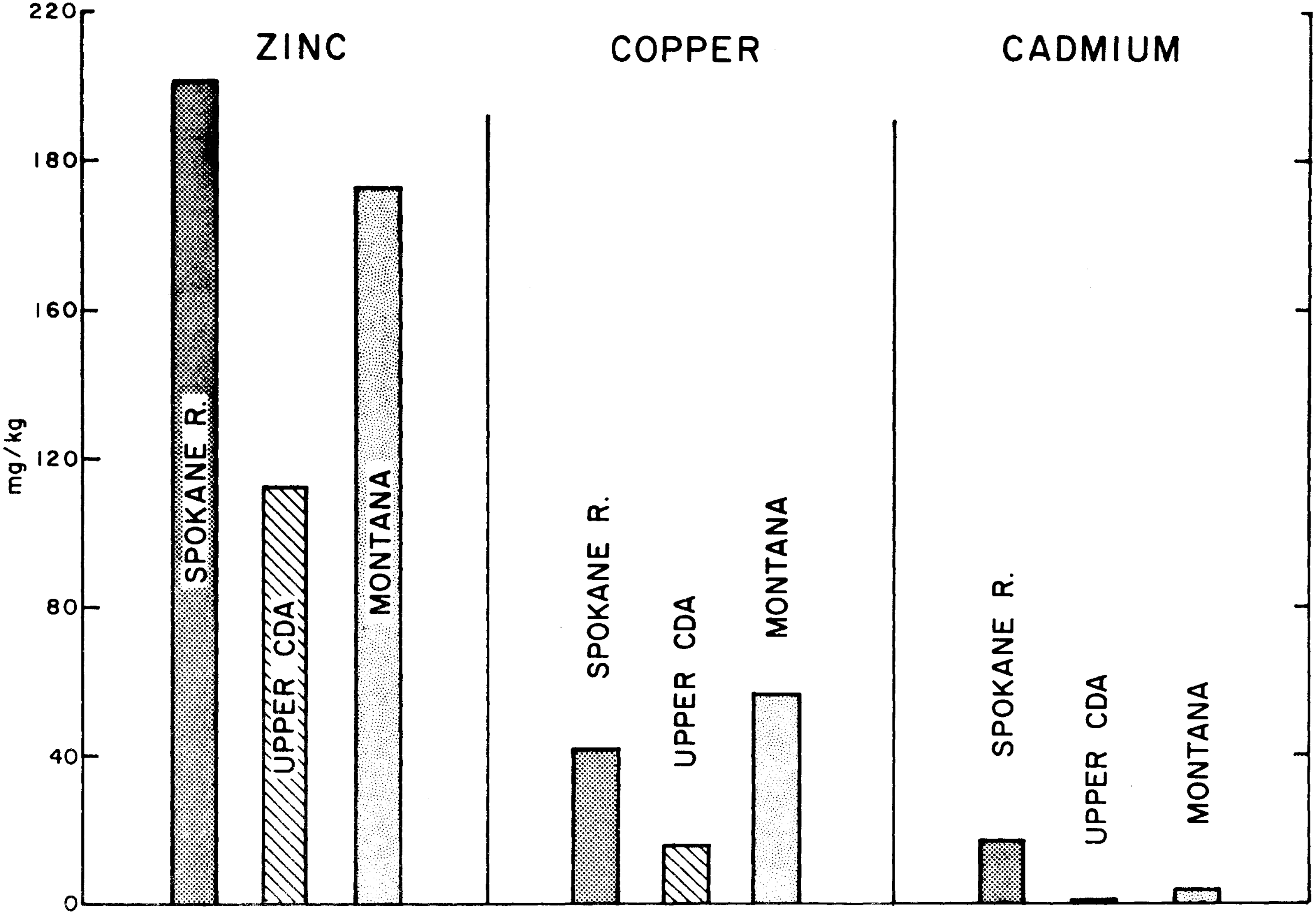

Figure 88. Comparison of Several Metals in Fishes from Mining Areas.

A comparison of metal content in tissues of black crappie (Pomoxis Nigro-maculatus), tench (Tinca tinca), bullhead (Ictalurus melas), yellow perch (Perca flaversceus) and sculpin (Cottus cognatus) was made on fishes from Lake Coeur d'Alene, the Spokane River and Tory Lake (Figure 89). Concentrations varied greatly, with trout being the highest of the six groups. This may be due to the fact that larger trout are predacious and are functioning at a higher trophic level. The fact that they feed directly on algae-eating insects also may account for the fact that they demonstrate higher levels of metals, especially Zn, in their tissues. Tables 49 to 53 contain data on additional metals in fish tissues as measured by neutron activation methods.

Ecological Implications

Water quality criteria (1968) suggest limits of metal exposure for aquatic organisms at 1/100 or less of the 96-hour TL_m. The zinc TL_m for trout ranges from .01 mg/1 in very soft water to 4.0 mg/1 in hard fresh water (Skidmore, 1964). As previously mentioned, Sappington (1969), working with cutthroat fingerlings and North Fork water, found a 96-hour TL_m of .09 mg/1 for Zn. Assuming, then, that the TL_m for brook and rainbow trout would not be significantly different from that for cutthroat, fishes in Coeur d'Alene Lake and the Spokane River are surviving in a concentration roughly 5 times that amount considered to be a median lethal dosage. Either the fishes have become acclimated to high Zn concentrations or our measurements of Zn in the Coeur d'Alene-Spokane River system include some nontoxic forms--perhaps bound to colloidal particles, or organic matter, as suggested by our laboratory study on Zn uptake (Bourg, 1974).

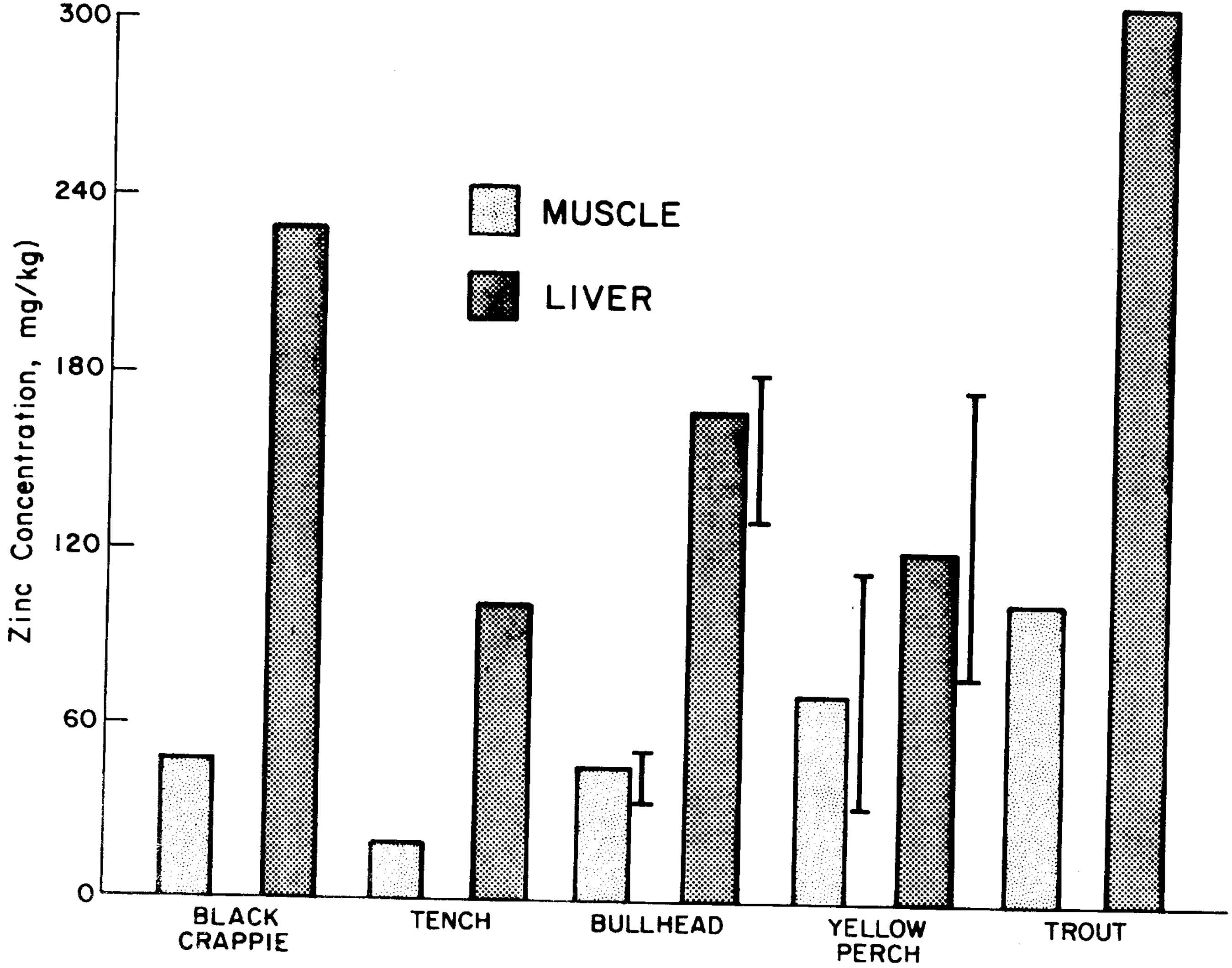

Figure 89. Comparison of Zinc Concentration in Tissues of Several Species of Fishes Within the Study Area.

Table 49. NEUTRON ACTIVATION ANALYSIS OF FISH TISSUES FROM THE UPPER COEUR D' ALENE RIVER DRAINAGE

(Mean Concentration of Metals (mg/kg) in Fish Tissues by Location

Location/Species	Length (cm)	Weight [g(wet)]	Organ	Ce	Se	Hg	Th	Cr	Zr	Cs	Ni	Tb	Sc	Rb	Fe	Zu	Ta	Co	Eu	Sb
Jordan Creek)F-1) Cut-throat	15.25	47.5	Liver	1.9	3.03	1.40	.464	1.43	--	1.10	--	--	.379	--	1674	149	--	.942	--	.668
			Fillet	--	--	--	--	.97	--	.730	--	--	.006	--	92	36	--	.222	--	--
			Heart	--	.46	.38	--	--	--	.978	--	--	.012	--	761	91	--	.346	--	.088
Tepee Creek (F-2) Cut-throat	17.14	58.5	Liver	1.15	1.8	.925	.145	8.35	--	.100	--	--	.222	--	1069.2	136	.585	.872	.032	--
			Fillet	.49	.47	.310	.129	5.27	--	.067	--	--	.133	--	480	40	--		.037	.090
			Heart	--	--	--	--	--	--	--	--	--	--	--	680	71	--	--	--	--
Trail Creek (F-3) Cut-throat	17.8	67	Liver	1.19	2.2	.784	.181	8.4	--	.214	--	.05	.251	--	1165	139	--	.808	.038	.249
			Fillet	--	--	--	--	--	--	--	--	--	--	--	128	53	--	--	--	--
			Heart	--	--	--	--	--	--	--	--	--	--	--	420	43	--	--	--	--
Shoshone Creek (F-4) Cut-throat	15.88	58	Liver	--	3.6	1.37	--	9.4	--	.098	.31	--	.026	--	1078	156.8	--	1.045	--	1.637
			Fillet	--	.4	.31	--	--	--	.090	--	--	.015	--	204	41	--	--	--	.105
			Heart	--	2.1	.84	.2	7.7	--	.239	.11	--	.22	--	1289	98	--	.823	.050	.246
South Fork Coeur d' Alene (F-5) Cut-throat	17.8	88	Liver	1.45	7.7	3.60	.159	12.96	--	.112	--	--	.195	11.89	1586.7	200.5	--	.629	.026	.215
			Fillet	.27	.80	.37	.06	4.20	--	.055	--	--	.065	6.34	316.3	18.1	--	.215	.012	.092
			Heart	.58	2.11	1.41	.128	8.04	--	.119	--	--	.170	8.7	1158.9	892	--	.468	.018	.173

Table 50. NEUTRON ACTIVATION ANALYSIS OF FISH TISSUES FROM THE LATERAL AND COEUR D'ALENE LAKES REGION

(Expressed as mg/kg)

Species	Length (cm)	Weight (wet)	Organ	Lu	Se	Hg	Th	Cr	Ba	Sr	Cs	Ni	Sc	Rb	Fe	Zn	Ta	Co	Eu	Sb
Medicine Lake																				
Tench	25.40	262.3g	Liver	--	2.43	.82	--	1.193	--	--	1.035	--	.004	14.1	801	97	--	.387	.007	.230
			Fillet	--	.62	.91	--	1.54	--	--	.149	1.7	.004	12.0	121	34	--	.203	--	.178
			Heart	--	2.26	1.1	--	4.43	--	--	.584	--	.010	9.0	1106	154	--	.919	--	.439
Yellow Perch	25.40	220.3g	Liver	.13	2.60	2.6	--	2.87	--	--	1.364	10.0	.009	13.9	722	125	--	.284	.024	.134
			Fillet	--	.65	2.9	--	2.21	--	--	3.957	--	.007	15.0	120	32	--	.155	--	.167
			Heart	--	2.14	4.15	--	4.83	--	--	7.691	9.5	.020	12.1	940	200	--	.602	.02	.662
Black Crappie	25.40	131 g	Liver	.04	3.1	2.05	--	1.67	--	--	4.12	2.8	.019	7.2	667	235	--	.523	.008	.323
			Fillet	--	.93	.96	--	2.16	--	--	5.5	--	.007	8.4	132	74	--	.114	--	.386
			Heart	--	4.5	2.0	--	1.84	--	--	20.6	--	.017	22.5	1800	357	--	1.02	--	2.9
Black Bullhead	25.40	273 g	Liver	--	4.5	1.6	.122	3.86	--	--	11.32	45	.051	12.0	5297	196	--	.523	.021	.935
			Fillet	--	1.5	1.34	--	1.68	--	--	.897	--	.008	18.0	313	98	--	.226	.017	--
			Heart	--	2.02	.871	--	3.69	--	--	1.690	4.2	.018	8.4	1844	104	(23)	.712	.016	.431
			Kidney	--	16.17	5.6	.086	1.829	--	--	4.161	--	.014	37.0	1299	344	--	3.93	.023	.904
Sucker	33.02	561 g	Fillet	--	78.0	53.0	22.1	--	--	--	22.5	--	--	--	--	--	--	--	--	--
			Heart	--	5.0	1.83	--	2.00	--	28.4	13.8	--	.005	10.7	1057	210	--	.283	--	.443

TABLE 50. (Continued)

Species	Length (cm)	Weight (wet)	Organ	Lu	Se	Hg	Th	Cr	Ba	Sr	Cs	Ni	Sc	Rb	Fe	Zn	Ta	Co	Eu	Sb
Thompson Lake																				
Yellow Perch	13.34	32 g	Liver	--	2.2	.773	--	20.0	--	--	.356	--	.012	6.0	851	115	--	.693	.015	.867
			Fillet	--	2.0	1.906	--	6.49	--	--	3.44	--	.011	24.0	574	116	--	.521	--	.451
			Heart	--	3.2	1.407	--	19.2	--	--	8.11	--	.059	19.0	1864	187	--	2.30	--	1.701
Yellow Perch	12.7	19 g	Liver																	
			Fillet																	
			Heart																	
Coeur d'Alene Lake																				
Yellow Perch	15.24	47 g	Liver	--	2.6	3.58	.141	4.72	--	--	2.63	--	.158	21.2	840	178	--	.869	.036	1.084
			Fillet	--	0.9	.847	--	5.79	--	--	.341	4.2	.012	28.8	258	51	--	.542	.014	.484
			Heart	--	2.4	1.40	.098	16.6	--	--	3.98	--	.041	23.0	999	143	.095	1.60	.043	1.189
			Brain	--	1.5	.965	--	10.8	--	--	2.71	--	.033	23.3	678	357	--	1.16	.060	.835
Yellow Perch	17.15	68 g	Liver	--	3.7	1.24	--	3.18	--	--		--								
			Brain																	
Yellow Perch	22.23	165 g	Liver	--	3.7	1.24	--	3.18	--	--	.082	--	.010	5.1	473	128	--	.549	.015	.213
Yellow Perch	24.77	279 g	Fillet	--	1.2	.792	--	3.75	--	--	1.76	--	.010	8.2	208	50	--	.465	.015	.339
			Brain	.017	1.2	.586	--	8.17	--	--	13.8	--	.020	2.8	417	145	.060	1.589	--	.915

Table 51. NEUTRON ACTIVATION ANALYSIS OF FISH TISSUES FROM UPPER SPOKANE RIVER

(Expressed as mg/kg)

Species	Length (cm)	Weight [g(wet)]	Organ	Ce	Se	Th	Cr	Hf	Ba	St	Zr	Cs	Ni	Tb	Sc	Rb	Fe	Zn	Ta	Co	Eu	Sb
Rainbow	34		Liver	.103	1.64	8.976	.787	--	--	--	--	.044	--	--	.003	9.76	369.7	230.6	--	.7	--	.035
			Fillet	--	--	--	3.305	--	--	--	--	1.15	--	--	.003	27.67	43.1	56.75	--	.09	--	.134
			Heart	--	1.65	--	.57	--	--	--	--	.066	--	--	.002	11.16	418.87	161.34	--	.36	--	.034
			Spleen	--	--	--	5.596	--	24.43	--	--	.80	--	--	.007	20.55	2800.10	370.60	--	.5	--	.174
Rainbow	30	281	Liver	--	4.73	--	1.278	--	--	--	--	.042	--	--	.007	10.7	1038	294.78	--	.4	--	.101
			Fillet	--	.77	--	1.03	--	--	--	--	.058	--	--	.002	12.86	30.67	70.57	--	.05	--	.081
			Heart	--	1.61	--	.617	--	--	--	--	.061	--	--	.002	11.84	421.38	162.28	--	.38	.068	.043
			Kidney	--	6.94	--	.769	--	26.7	--	--	.055	--	--	.004	17.69	2072.25	395.4	--	.7	--	.075
Rainbow	16	48	Liver	--	2.79	--	--	--	--	--	--	.024	--	--	--	8.98	827.68	358.3	--	.45	--	.053
			Fillet	--	.78	--	--	--	--	--	--	.032	--	--	.003	9.24	28.66	30.7	--	.07	--	.060
			Heart	1.78	2.33	--	--	--	--	--	--	.183	--	.072	.003	19.39	1211.07	321.	--	1.11	.068	1.362
Rainbow	18	57	Liver	--	2.04	--	.844	--	--	--	--	--	--	--	--	5.38	486	442	--	.243	--	--
			Fillet	--	.68	--	.440	--	--	--	--	.029	--	--	--	9.83	16.81	37	--	.043	--	.004
			Heart	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Brook	15	38	Liver	--	1.55	--	1.6	--	--	--	--	.014	--	--	--	5.6	255.8	297	--	.197	--	.033
			Fillet	--	.77	--	1.7	--	--	--	--	.038	--	--	.001	9.8	22.9	76	--	.072	--	.094
			Heart	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
			Eggs	--	2.67	--	.7	--	--	--	--	.059	--	--	--	8.5	293	535	.022	.465	--	.200
Rainbow	20	94	Liver	--	2.46	--	1.14	--	--	--	--	.043	--	--	.005	9.56	440.6	257.6	--	.311	--	.080
			Fillet	--	.65	--	1.15	--	--	--	5.08	.043	--	--	.002	14.62	30.1	258.8	--	.085	--	.112
			Heart	--	1.24	--	2.6	--	--	--	--	.070	--	--	.005	11.46	373.6	35	--	.412	.015	.110

Table 52. NEUTRON ACTIVATION ANALYSIS OF FISH TISSUES FROM UPPER SPOKANE RIVER

(Expressed as mg/kg)

Species	Length (cm)	Weight [g(wet)]	Organ	Ce	Se	Th	Cr	Hf	Ba	St	Zr	Cs	Ni	Tb	Sc	Rb	Fe	Zn	Ta	Co	Eu	Sb
Rainbow	21	106	Liver	.11	1.77	--	15	--	--	--	--	.043	--	--	.006	9.2	595.3	363	--	.19	--	.085
			Fillet	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
			Heart	--	1.85	83	2.67	--	--	--	--	.058	--	--	.005	7.2	366.97	255	--	.23	--	.213
			P.Caeca	1.01	1.42	178	3.17	--	--	--	--	.146	--	--	.132	10.3	528.2	1386	--	.22	24.7	.120
Rainbow	35	467	Liver	.12	2.34	12.11	.75	--	--	--	--	.043	--	--	.003	8.98	369.67	235.36	--	.69	--	.024
			Fillet	--	1.61	--	3.06	--	--	--	--	.116	--	--	.003	27.40	40.65	56.38	--	.11	--	.094
			Spleen	--	3.68	--	5.25	--	29.25	--	--	.077	--	--	.006	18.92	2664.00	364.84	--	.52	--	.095
			Kidney	--	6.59	--	.08	--	30.90	--	--	.064	--	--	.004	17.29	2017.12	400.84	--	.74	28.61	.071
Rainbow	32	280	Liver	--	4.63	--	1.2	--	--	--	--	.044	--	--	.006	10.82	1013.4	297.56	--	.42	--	.105
			Fillet	--	.799	--	1.0	--	--	--	--	.066	--	--	.005	12.40	30.82	70.73	--	.05	12.31	.070
			Heart	--	1.650	--	.57	--	--	--	--	.066	--	--	.001	11.16	418.17	161.54	--	.36	--	.034
			Kidney	--	6.59	--	.76	--	--	--	--	.064	--	--	.004	17.29	2017.12	400.83	--	.73	28.60	.071
Rainbow	16	58	Liver	.52	2.69	--	9.32	--	--	--	--	--	--	--	.017	11.08	875.27	438.17	--	.99	17.69	.482
			Fillet	--	8.96	--	.91	--	--	--	--	.081	--	--	.002	11.79	28.63	50.55	--	.13	9.18	.061
			Heart	--	1.74	--	2.67	--	--	--	--	.107	--	--	.008	10.21	429.68	301.11	--	.64	16.71	.275
Rainbow	19	99	Liver	--	2.76	--	1.74	--	--	--	--	.042	--	--	.006	8.26	1035.33	274.67	--	.23	--	--
			Spleen	--	1.90	30.30	.83	--	--	--	--	--	--	--	.005	8.93	1050.16	242.19	--	.23	13.18	.137

Table 53. NEUTRON ACTIVATION ANALYSIS OF FISH TISSUES FROM UPPER SPOKANE RIVER (Expressed as mg/kg)

Species	Length (cm)	Weight [g(wet)]	Organ	Ce	Se	Th	Cr	Hf	Ba	St	Zr	Cs	Ni	Tb	Sc	Rb	Fe	Zn	Ta	Co	Eu	Sb
Upriver Dam																						
Brook Trout	20	90	Liver	.467	1.51	--	.7	--	--	--	--	.169	--	--	.004	8.05	445	142	--	.344	.003	.005
			Fillet	.7	1.94	--	1.02	--	--	--	--	.425	--	--	.007	26.9	53	87	--	.196	.014	.234
			Heart	--	2.25	--	3.06	--	--	--	--	.458	--	--	.011	14.8	640	363	--	.85	--	--
Rainbow Trout	20	94	Liver	--	4.49	--	1.89	--	--	--	--	.239	--	--	.005	9.6	897	357	--	.2	--	.102
			Fillet	--	.76	--	7.24	--	--	--	--	.188	--	--	--	--	--	--	--	--	--	--
			Heart	--	--	--	--	--	--	--	--	--	--	--	.005	9.94	64.9	49	--	.08	--	.346
			Kidney	--	3.34	--	4.02	--	--	--	--	.201	--	--	.010	10.67	768.3	548.09	--	.55	---	.163
Rainbow Trout	36	567	Liver	--	13.0	.036	5.81	--	--	--	--	.80	--	--	.037	22.59	1860.5	264	--	.484	--	.324
			Fillet	--	.85	--	2.76	--	--	--	6.8	.665	--	--	.005	19.89	67.07	29	--	.21	--	.210
			Heart	--	2.06	--	3.89	--	--	--	--	1.073	--	--	.003	20.32	550.20	266	--	.69	--	.094
			Brain	--	--	.023	2.8	--	--	--	--	--	--	--	.023	--	91.72	42	--	.07	.014	.042
Rainbow Trout	27	274	Liver	--	6.91	--	1.63	--	--	--	--	.990	--	.035	.017	22.27	12.45	324	--	.529	.013	.100
			Fillet	--	1.04	--	2.45	--	--	--	--	.631	--	--	.010	17.16	425	54	--	.152	--	.097
			Heart	--	2.27	--	1.32	--	--	--	7.9	.955	--	--	.004	18.476	657	194	--	.496	--	.049
Brook Trout	23	177	Liver	--	4.32	--	1.24	--	--	--	--	.103	--	--	--	9.593	836.3	176	--	1.02	--	.079
			Fillet	--	1.48	--	1.84	--	--	--	--	.185	2.08	--	.003	13.399	84.2	38	--	.189	--	.068
			Heart	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Brook Trout	18	81	Liver	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
			Fillet	--	1.31	--	1.73	--	--	--	--	.199	--	--	.001	13.06	37.64	34	.01	.122	--	.056
			Heart	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
			Eggs	--	4.13	--	.96	--	--	--	--	.188	--	--	.002	9.65	349.9	504	--	.906	--	.004
Brook Trout	22	122	Liver	--	3.79	--	1.47	--	--	--	--	.209	--	--	--	--	--	300	--	.70	--	.100
			Fillet	--	1.27	--	.95	--	--	--	--	.282	--	--	.002	15.65	29	44	--	.10	--	.062
			Heart	--	2.02	--	9.09	--	--	--	--	.233	--	--	--	16.72	--	250	--	.71	--	.127

SUMMARY AND CONCLUSIONS

Comprehensive limnological, water quality, productivity and substrata investigations have been made of the Coeur d'Alene drainage, Coeur d'Alene Lake and the Spokane River. These investigations were made in an attempt to answer questions as to the passage of metallic elements through the aquatic food chain in the study area as well as to determine the critical factors involved in the poor recovery of benthic populations of the South Fork and main stem of the Coeur d'Alene River. Additional work was carried out to determine the water quality of these areas and the Spokane River. Extensive studies also were made upon the substrata and limiting factors of macroinvertebrates of the Upper Spokane River. The following paragraphs summarize the findings of the joint investigators.

Coeur d'Alene River

Artificial substrates (baskets) placed in the unpolluted portions of the Coeur d'Alene developed abundant and diverse macroinvertebrate fauna comparable to those collected from natural substrata by Surber sampler.

When artificial substrate devices were placed in the polluted portion of the Coeur d'Alene River (South Fork, main stem at .4 and .8 mi below confluence), only a sparse fauna developed. Variation of fauna between stations in the polluted portions of the river indicated a possible growth-limiting factor due to considerable amounts of sands at Station 3 which may have resulted in compaction and loss of suitable habitat. Colonized baskets from the relatively unpolluted North Fork were placed in the South Fork on September 15, 1973. Within two weeks the existing community was reduced from 227 individuals (18 species) to 49 individuals (4 species), leading the investigators to believe that water quality factors are still the primary reason for lack of diversity and inhibition of development of a healthy benthic macroinvertebrate community in the South Fork and main stem of the Coeur d'Alene River.

Lateral Lakes

Flooding of the Coeur d'Alene River during the spring highwater period transports heavy metals, especially Zn, into the lateral lakes bordering the river. Zinc concentrations in the water were highest near the lake inlets.

Zinc, Cu, Cd and Pb in sediments of the lakes exceeded background levels several-fold, especially near the inlets. It is believed, however, that these metals strongly adsorbed to the sediments and did not adversely affect the biota at the time of study.

Metal concentrations in fishes from the lakes were higher than those tested from a control lake in the St. Joe drainage. There appeared to be greater Zn concentrations in the muscle tissue of omnivorous fish such as the bullhead than in the same tissues of piscivorous fish such as the largemouth bass. The fishes seemed to be exerting some homeostatic control over the metal level in their tissues.

Coeur d'Alene Lake

The overall water quality of the Coeur d'Alene Lake appeared to be relatively the same as we found in our earlier study (Funk, Rabe, Filby *et al.*, 1973) based upon routine water sampling during coring operations and on data gathered from a water quality station maintained at the lake outlet.

Nineteen sediment cores were obtained from the lengthwise axis of the lake and from selected bays. A layer of heavy metals 80-30 cm in thickness occurred in the Coeur d'Alene delta region and lake proper. This layer decreased in thickness as one traversed the lake from off the delta region toward the outlet, where the layer is reduced to 5 cm. Coring operations from the delta region of the lake toward the southern end revealed the same phenomenon occurred to a lesser extent to a point between the area off Conkling Park and Chatcolet Lake. This layer of heavy metals could constitute a hazard to aquatic life if Coeur d'Alene Lake eutrophies to the point of anaerobic conditions in the hypolimnion.

Studies conducted on Coeur d'Alene River and Lake waters showed that 83 to 94% of the Zn in the water was in a dissolved state (Seamster and Filby, 1974). They determined that soluble Zn was found in cationic form 51 to 98%, anionic form 1 to 5% and in neutral form 2 to 44% during these measurements. Laboratory studies of this investigations have shown that the clays in the sediments of the river and lake system may act as a buffering system, contolling the Zn concentration of the overlying waters.

Spokane River

The water quality of the upper Spokane River is considered to be good based upon extensive environmental engineering and limnological investigations. The bacteriological condition of the upper four of the river stations sampled met Class A standards, and the lower four stations met Class B standards of the State of Washington.

The biological productivity of the Spokane River is largely controlled by the water quality of the Coeur d'Alene Lake as well as substrate, temperature and flow of the river. Nutrient addition to the river as it flows toward the city of Spokane increases the productivity of the lower four stations, especially at the Plantes Ferry station.

Heavy metals such as Zn, Cu and Pb appear to be concentrated to relatively high amounts in algae, aquatic macrophytes and other vegetation growing along the river. Algae- and detritus-consuming macroinvertebrates such as mayflies and stone flies pass these metals along to the fishes, especially trout, because of the trout's predilection for these organisms. However, there appears to be a reduction of concentration of metals in tissues at each trophic level as one moves up the food chain. The organisms appear to be actively excreting the metals. In the fishes the filter bodies such as the kidneys and liver concentrated the metals several-fold over that of other tissues and therefore tend to confirm this assumption. Nonetheless, the level of Zn, for example, in the muscle tissue of Spokane River fishes may be two to three times that in muscle tissue of the same species of fishes taken from undisturbed streams high in Coeur d'Alene drainage. For these reasons it has been concluded by the investigators that additional efforts should be made to curtail and control seepage from tailing ponds as well to reduce and eventually control wastes and nutrient runoff in the Coeur d'Alene and Spokane Rivers drainage basins. The area encompassed by this study represents extremely valuable recreation, wildlife and fisheries resources as well as sources of food and water for human consumption.

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APPENDICES

Table A-1. Water Quality Data for Four Stations in the Coeur d'Alene River from July 1, 1973 to October 5, 1973.

Date Station	Discharge[1] cfs	pH	O_2 mg/1	O_2 % Sat.	Total Alkalinity mg/1	Temperature C	
						air	water
7/1/73							
1	488	7.3	8.8	96	20	24	15
2	220	7.0	9.5	103	18	24	15
3	708	7.2	9.7	107	14	26.5	16
4b	-	7.1	9.5	107	16	24	17
8/1/73							
1	259	7.4	9.0	105	18	27	18
2	141	7.0	9.9	125	12	30	23
3	400	7.2	9.5	111	14	31	19
4b	-	7.2	8.8	103	14	27	19
8/16/73							
1	221	7.2	8.4	92	18	22	16
2	115	6.5	10.2	112	8	22	15.5
3	336	6.8	8.5	92	12	22	15.5
4b	-	6.8	7.9	86	12	20.5	15.5
8/30/73							
1	200	7.2	8.5	91	16	21	15
2	93	6.2	10.1	109	3	21	15
3	293	7.0	7.2	78	12	18	15
4b	-	7.0	8.0	86	12	18	15
9/13/73							
1	179	7.2	8.6	91	18	22	14
2	83	6.2	9.8	106	5	22	15
3	262	6.7	9.4	97	12	22	13
4b	-	6.7	8.8	93	12	22	14
10/5/73							
1	227	7.2	-	-	16	11	9
2	101	5.0	-	-	4	11	9
3	328	6.6	10.2	96	10	11	9
4b	-	6.6	9.4	85	10	7	7

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[1] Discharge data from U.S. Geological Survey guaging stations at Enaville (North Fork) and Smelterville (South Fork). Discharge at station 3 was sum of that at 1 and 2; discharge at station 4 was unknown as river divided around an island.

Table A-1. Water Quality Data for Five Stations in the Coeur d'Alene River from August 1, 1973 to September 13, 1973.

Date Station	NH_3-N mg/l	NO_3-N mg/l	O-PO_4 mg/l	Total PO_4 mg/l	SO_4 mg/l
8/1/73					
1b	0.004	0.013	0.009	0.00	2
2a	.14	.147	.10	1.10	157
3b	.01	.07	.09	.52	58
4a	.06	.061	.09	.46	51
4b	-	-	-	-	-
8/16/73					
1b	0.005	0.015	0.005	0.03	3
2a	.26	.257	.11	2.00	180
3b	.115	.096	.046	.58	64
4a	.125	.10	.046	.52	67
4b	.12	.102	.05	.55	67
8/30/73					
1b	0.00	0.147	0.015	0.05	2
2a	.28	.245	.14	2.00	200
3b	.095	.095	.05	.70	73
4a	.11	.099	.04	.65	77
4b	.12	.113	.06	.73	77
9/13/73					
1b	0.01	0.02	0.01	0.08	3
2a	.30	.339	2.04	2.00	220
3b	.14	.146	.23	1.65	81
4a	.16	.151	.32	1.75	90
4b	.15	.146	.24	1.68	91

Table A-1. Water Quality Data for Four Stations in the Coeur D'Alene River from July 1, 1973 to October 5, 1973.

Date Station	Turbidity mg/l	Conductivity µmhos	Zn mg/l	Cd mg/l	Cu mg/l	Pb mg/l	Fl mg/l
7/1/73							
1	0	55	0.01	0.01	0.05[1]	0.05	
2	17	225	5.50	.08		.05	
3	9	120	1.60	.01		.05	
4b	9	115	1.55	.04		.05	
8/1/73							
1	7	63	.01	.01		.05	
2	30	380	16.00	.17		.05	
3	11	180	3.30	.04		.05	
4b	11	152	3.10	.02		.05	
8/16/73							
1	3	67	.01	.01		.05	
2	42	415	23.00	.35		1.00	
3	14	190	4.30	.10		.50	
4b	12	200	4.70	.14		.80	
8/30/73							
1	7	60	.01	.01		.05	
2	35	440	16.00	.26		1.00	
3	9	218	4.30	.10		.50	
4b	18	220	4.60	.10		.50	
9/13/73							
1	2	60	.01	.01		.05	0.065
2	51	422	15.00	.26		2.80	6.8
3	27	228	4.10	.03		.20	-
4b	35	240	4.30	.10		.50	2.4
10/5/73							
1	-	-	.01	.01		-	
2	-	-	14.00	.20		-	
3	-	-	3.20	.03		-	
4b	-	-	3.90	.07		-	

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[1] Cu .05 mg/l for all dates and stations.

Table A-2. Macroinvertebrates in Mundie/Basket Samplers
During Summer, 1973 at Four Stations in the Coeur d'Alene River.

	1	2	3	4
EPHEMEROPTERA				
Epeorus	4/			
Rhithrogena				
Cinygma				
Ephemerella serrata				
E. needhami	5/			
E. walkeri				
Baetis bicaudatus				
Baetis tricaudatus	1/			
Pseudocloeon	5/			
Centroptilum				
Paraleptophlebia heteronea	26/			
Potamanthus				
PLECOPTERA				
Pteronarcella regularis	1/			
Pteronarcys californica				
Claasenia sabulasa	4/			
Acroneuria				
Arcynopteryx aurea				
Other Perlodidae	6/			
Chloroperlinae	8/			
TRICHOPTERA				
Hydropsyche	43/			
Arctopsyche				
Glossosoma	1/			
Rhyacophila	1/			
Brachycentrus				
Glyphopsyche				
Limnophilidae sp. A	5/			
Lepidostoma	14/			
Ochrotrichia	1/			
Mystacides				
COLEOPTERA				
Optioservus	45/			
Zaitzevia	15/			
Brychius				
Oreodytes				
DIPTERA				
Psychoda				
Atherix variegata	22/			
Antocha	1/			
Tipulidae sp. A	1/			
Empididae				
Tabanidae				
Simulidae	2/			
Orthocladinae	5/			
Chironominae sp. A	1/			
Chironominae sp. B	2/			
Tanypodinae	1/			
HYDRACARINA				
OLIGOCHAETA				

Table A-3. Macroinvertebrates in Surber/Basket Samplers Collected on October 5, 1975 at Four Stations in the Coeur d'Alene River.

	1	2	3	4
EPHEMEROPTERA				
Epeorus				
Rhithrogena	17/22			
Cinygma				
Ephemerella serrata	21/159		/1	
E. needhami				
E. walkeri	/1			
Baetis bicaudatus	/6			
Baetis tricaudatus	1/3		/1	
Pseudocloeon	4/			
Centroptilum				
Paraleptophlebia heteronea	12/			
Potamanthus				
PLECOPTERA				
Pteronarcella regularis	1/4			
Pteronarcys californica				
Claasenia sabulasa				
Acroneuria	1/			
Arcynopteryx aurea	1/1			
Other Perlodidae	7/25		/2	
Chloroperlinae	5/3			
TRICHOPTERA				
Hydropsyche	54/165		1/7	/11
Arctopsyche	1/1			
Glossosoma	1/5			
Rhyacophila	1/		/1	
Brachycentrus	2/4			
Glyphopsyche				
Limnophilidae sp. A				
Lepidostoma	/2			
Ochrotrichia	/1			
Mystacides				
COLEOPTERA				
Optioservus	15/9			
Zaitzevia	34/3			
Brychius	2/4		/1	
Oreodytes		/1		
DIPTERA				
Psychoda				
Atherix variegata	11/7		/1	
Antocha	1/7			
Tipulidae sp. A	1/			
Empididae			/1	
Tabanidae				
Simulidae	1/41		/1	
Orthocladinae	13/101	8/17	5/35	1/4
Chironominae sp. A	/21	/4	1/22	
Chironominae sp. B	1/			
Tanypodinae	1/		/4	
HYDRACARINA				
OLIGOCHAETA				

Table A-4. Macroinvertebrates in Surber/Basket Samplers Collected on August 1, 1973 at Four Stations in the Coeur d'Alene River.

	1	2	3	4
EPHEMEROPTERA				
Epeorus	3/51			3/
Rhithrogena	-/28			
Cinygma	9/16			2/2
Ephemerella serrata	34/32			1/
E. needhami	14/34			
E. walkeri	-			
Baetis bicaudatus	2/4		/2	
Baetis tricaudatus	12/120	3/5	/3	/3
Pseudocloeon	6/25		/1	3/
Centroptilum	-/25			
Paraleptophlebia heteronea	-			/2
Potamanthus	-			
PLECOPTERA				
Pteronarcella regularis	5/18		/3	
Pteronarcys californica	-			
Claasenia sabulasa	-		/1	
Acroneuria	9/1			
Arcynopteryx aurea				
Other Perlodidae	15/15		/2	4/2
Chloroperlinae	4/28		/2	
TRICHOPTERA				
Hydropsyche	64/936		6/18	7/1
Arctopsyche	/6			
Glossosoma	46/3		/2	
Rhyacophila			/1	
Brachycentrus	4/2			
Glyphopsyche				
Limnophilidae sp. A	4/1			
Lepidostoma				
Ochrotrichia	/21			
Mystacides	/2			
COLEOPTERA				
Optioservus	28/14		2/	6/1
Zaitzevia	129/1		/1	
Brychius	10/19		/56	
Oreodytes	1/4	51/43		/4
DIPTERA				
Psychoda		/3		
Atherix variegata	20/14	/1	2/55	/2
Antocha	16/16			
Tipulidae sp.A				
Empididae				/1
Tabanidae		2/		
Simulidae	5/129		/19	2/
Orthocladinae	34/869	51/139	17/109	67/321
Chironominae sp. A		5/	7/45	
Chironominae sp. B	56/342	15/20		50/18
Tanypodinae	2/263	1/8	2/19	2/287
HYDRACARINA	/17			
OLIGOCHAETA		1/2		

Table B-1. Analysis of Variance Summary Tables for Metals in Yellow Perch From the Coeur d'Alene River Valley Lakes (*Significant at the 0.5 level, ** significant at the 0.1 level).

ZINC--LIVER

SOURCES OF VARIATION	D.F.	SUM OF SQUARES	MEAN SQUARE	F
among lakes	7	112,683.74	16,097.68	4.088**
within lakes	50	196,881.28	3,937.63	
TOTAL	57	309,565.02		

ZINC--MUSCLE

SOURCES OF VARIATION	D.F.	SUM OF SQUARES	MEAN SQUARE	F
among lakes	7	18,217.32	2,602.47	11.33**
within lakes	49	11,252.77	229.65	
TOTAL	56	29,470.09		

COPPER--LIVER

SOURCES OF VARIATION	D.F.	SUM OF SQUARES	MEAN SQUARE	F
among lakes	6	5,448.66	908.11	4.029**
within lakes	26	5,860.64	225.41	
TOTAL	32	11,309.30		

COPPER--MUSCLE

SOURCES OF VARIATION	D.F.	SUM OF SQUARES	MEAN SQUARE	F
among lakes	7	2.55	0.36	13.812**
within lakes	40	1.05	0.03	
TOTAL	47	3.60		

CADMIUM--LIVER

SOURCES OF VARIATION	D.F.	SUM OF SQUARES	MEAN SQUARE	F.
among lakes	7	19,778.81	2,825.54	59.56
within lakes	44	2,087.07	47.43	
TOTAL	51	21,865.88		

CADMIUM--MUSCLE

SOURCES OF VARIATION	D.F.	SUM OF SQUARES	MEAN SQUARE	F
among lakes	7	2.04	0.29	3.089*
within lakes	37	3.49	0.094	
TOTAL	44	5.53		

Table B-2. Analysis of Variance Summary Tables for Metals in Species of Fishes from the Coeur d'Alene River Valley Lakes (* significant at the .05 level and ** significant at the .01 level).

ZINC--LIVER

SOURCES OF VARIATION	D.F.	SUM OF SQUARES	MEAN SQUARE	F
among species	4	142,149.59	35,537.40	8.78**
within species	81	327,959.17	4,048.88	
TOTAL	85	470,108.76		

ZINC--MUSCLE

SOURCES OF VARIATION	D.F.	SUM OF SQUARES	MEAN SQUARE	F
among species	4	12,384.79	3,096.20	3.19*
within species	82	79,525.41	969.82	
TOTAL	86	91,910.20		

COPPER--LIVER

SOURCES OF VARIATION	D.F.	SUM OF SQUARES	MEAN SQUARE	F
among species	4	15,154.12	3,788.53	18.70**
within species	52	10,534.46	202.59	
TOTAL	56	25,688.58		

COPPER--MUSCLE

SOURCES OF VARIATION	D.F.	SUM OF SQUARES	MEAN SQUARE	F
among species	4	37.25	9.31	4.97**
within species	67	125.61	1.88	
TOTAL	71	162.86		

CADMIUM--LIVER

SOURCES OF VARIATION	D.F.	SUM OF SQUARES	MEAN SQUARE	F
among species	4	2,185.73	546.43	4.62**
within species	64	7,564.47	118.19	
TOTAL	68	9,750.20		

CADMIUM--MUSCLE

SOURCES OF VARIATION	D.F.	SUM OF SQUARES	MEAN SQUARE	F
among species	4	3.70	0.910	$1.88^{\text{n.s.}}$
within species	46	22.28	0.484	
TOTAL	50	25.98		

(Tables C-1 to C-19, Analysis of Sediment Cores Driven Along the Lengthwise Axis and in the Bays of Coeur d'Alene Lake (Expressed as mg/kg unless otherwise noted).

Table C-1. Standard Chemical and Atomic Absorption Analysis of Core 6 (.7km off Bells Bay, 23.3m Water-depth).

Depth cm	% Water Content	pH	Eh	Total P	NH_3-N	Org N	Total Org C	Zn	Mn	Mg	Pb	Fe	Cu	Cd
3.5-10	90	4.2	410	2340	84	980		3160	2680	628	3600	17480	106.0	42.0
10-20	84	3.98	275	1440	84	2003		4480	2920	928	3420	24800	106.0	29.6
20-30	69	4.0	440	3600	252	868		1500	624	212	1040	11160	22.8	7.0
30-40	76	4.4	310	3040	168	2070		1280	488	183.2	42.0	11000	16.0	6.4
40-50	76	4.95	440	3600	196	2040		1340	148	167.6	41.0	7800	9.2	0.26
50-60	76	5.24	509	4200	280	2040		1040	136	167.6	23.2	9000	11.44	4.8
60-69	74	5.35	325	3500	280	2100		1240	152	168.8	42.0	10240	14.0	4.4

Table C-2. Standard Chemical and Atomic Absorption Analysis of Core 7 (Between Rockford Point and East Point, 34m Water-depth).

Depth cm	% Water Content	pH	Eh	Total P	NH_3-N	Org N	Total Org C	Zn	Mn	Mg	Pb	Fe	Cu	Cd
0-5	75	6.95	445		90			2328	1680	860	3660	34160	93.2	33.0
5-6	72	6.7	97		85			3448	2092	920	4080	33280	88.0	24.0
10-11	70	6.35	125					1600	1420	292	178.8	12000	16.4	1.34
15-16	72	6.3	125					1560	408	270.8	92.0	25480	12.8	4.0
20-21	70	6.3	180					1620	352	232	41.0	14200	10.4	0.476
25-26	69	6.45	145					1500	344	229.2	28.0	14880	10.4	0.20
30-31	64	6.15	169		280			1620	372	282	23.2	14960	12.0	0.320
35-36	64	6.4	140	5740	336			1548	340	243.2	23.2	14200	9.6	0.420
40-41	64	6.25	162	5100	252			1548	344	234	26.0	14400	9.2	0.340
45-46	64	6.44	145	4800	308			1280	304	216	36.0	13080	12.0	0.40
50-51	64	6.4	180	5340	364			1500	328	237.6	20.0	15080	12.0	0.40
55-56	50	6.3	160	5740	368			1560	336	274.8	12.0	15600	12.4	0.268
61-64	54	6.28	170	4700				1500	312	268.8	15.0	14600	8.0	0.296

Table C-3. Standard Chemical and Atomic Absorption Analysis of Core 8 (Midpoint between Half Round and Black Rock Bays, 44.2m Water-depth).

Depth cm	% Water Content	pH	Eh	Total P	NH_3-N	Org. N	Total Org. C	Zn	Mn	Mg	Pb	Fe	Cu	Cd
0-1	78	6.55	180	2150	90	1100		2220	560	480	1560	18200	34.8	39.2
5-6	44	6.95	133	1975	100			1920	1308	848	3400	36800	60.0	52.0
10-11	58	6.6	185	1980	110	1980		1440	508	308.8	340	17600	13.0	5.2
15-16	55	6.5	210	2135	140			1240	508	307.2	72.0	17600	12.0	0.932
20-21	54	6.4	195	2995	340	1440		36.8	1416	296.8	37.12	13800	12.8	0.752
25-26	56	6.4	230	3480	290	975		34.8	1432	294	22.8	12600	17.6	0.60
30-31	52	6.4	195	3200	270	1350		69	1368	252	22.2	13600	18.8	0.656
35-36	50	6.3	200	3250	270	1662		34.6	308	66	21.08	12240	17.04	0.596
40-41	54	6.45	170	3400	441			78.8	1280	256	18.2	15040	13.08	0.62
45-46	46	6.45	180	3700	444			32.8	1320	253.6	18.2	16400	13.08	0.62
50-51	48	6.5	165	3850	448			31.2	1220	233.6	19.2	15200	13.88	0.68
55-56	48	6.4	160	4120		1660		30.8	1290	256.8	18.8	15600	15.08	0.82
60-61	51	6.25	170	3430	450	1661		30.4	1200	253.6	22.8	15600	14.16	0.648

Table C-4. Standard Chemical and Atomic Absorption Analysis of Core 9 (Midlake, 1.2km off McDonald Point, 39.6m Water-depth).

depth cm	% Water Content	pH	Eh	Total-P	NO_3	Total Organic-C	Cd	Cu	Cr	Mn	Ni	Pb	Zn
0-2	60	7	720	2367	22	20,400		143	164	5420	39	ND	1810
4-6	63	6.8	685	3567	25	20,300		486	132.4	3440	36.6	69	2600
8-10	69	6.7	740	4933	20	19,800		31.8	123.8	3100	39	ND	3200
12-14	70	6.7	740	5467	16	20,300		18.6	104	1106	32.7	"	2520
16-18	71	6.6	720	5167	38	18,400		19.8	89.8	1106	27.4	"	178
20-22	71	6.7	740	5300	22	18,300		22.4	119.8	1070	42.4	"	122
24-26	71	6.65	760	3333	22	19,800		22.36	102	1052	33.8	"	102
28-30	70	6.6	750	5100	26	17,300		20.8	95.2	986	32	"	88
32-34	70	6.4	835	4667	18	17,000		22.4	110	970	36.3	"	90
36-38	68	6.8	765	4500	20	15,700		25	119	986	41.8	"	50
40-42	69	6.6	750	4567	28	17,900		24.9	90	682	36.8	"	278
44-46	70	6.75	770		27	15,800		23.4	102	884	40	"	98
48-50	70	6.6	780	3800	28	13,900		25.2	146.4	830	40.4	"	108
56-58	71	6.6	780	4400	22			25	126.8	921	41.8	"	104
60-62	71	6.65	720	3667	17			25	86.2	901	32	"	162
64-66	72	6.3	710			17,300		23	118.2	898	39	"	100
68-70	72	6.5	770	1867	32	19,500		22.36	100.6	853	33.8	"	98

Table C-5. Standard Chemical and Atomic Absorption Analysis of Core 11 (.9km off Tubbs Hill Light, 32.9m Water-depth).

Depth cm	% Water Content	pH	Eh	Total P	NH_3-N	Org. N	Total Org. C	Zn	Mn	Mg	Pb	Fe	Cu	Cd
0-5	83	6.45	85					3948	4228	780	3520	24400	78.80	32.8
5-10	88	6.25	160					560	2600	540	1000	10200	16.80	8.80
10-15	82	6.15	180					200	1212	520	254	8520	13.20	4.40
15-20	79	6.05	215					102	1188	600	160	8800	17.04	3.20
20-25	75	6.1	190					105	732	548	118	8480	16.20	2.28
25-30	72	6.25	220					100	700	520	106	9120	15.80	1.80
30-35	73	6.1	180					64.8	608	500	86	8200	16.12	1.44
35-40	68	6.0	225					54.8	592	500	62	9000	14.52	0.92
40-50	66	6.25	150					54.8	600	492	86	8480	16.12	1.20
50-60	65	6.4	135					48	648	516	62	8520	15.16	0.84
60-70	60	6.2	140					43.2	568	508	52	9400	15.80	0.68
70-80	58	6.0	170					37.48	532	500	28	8480	16.12	0.44
80-90	69	6.3	140					48	492	400	34.4	8480	15.28	0.48
90-100	55	6.4	170					33.48	480	420	30.6	7600	15.48	0.40
100-105	54	6.3	140					27.00	400	360	29.4	7400	15.60	3.00
at 105		5.8	190											

Table C-6. Standard Chemical and Absorption Analysis of Core 12 (Midpoint of Chatcolet Lake, 3m Water-depth).

Depth cm	% Water Content	pH	Eh	Total P	NH_3-N	Org. N	Total Org. C	Zn	Mn	Mg	Pb	Fe	Cu	Cd
2.5	81	181	5.7					44.5	210	12	29	2700	4.95	
6.5	15	185	5.9					72	101	13	5.5	2710	3.5	
12.5	79	196	5.9					83	75	19	4.95	1500	8.1	
17	64	199	5.6					139	135	22	7.5	4700	3.0	
22.5	68	240	5.5					153	133	18	5.0	4650	9	
26	61	250	5.5					141	140	29	8.5	4652	14.1	
32.5	60	445	5.7					113	126	39	7.0	4400	12.91	
36.5	64	451	5.9					141	301	33	7.1	6500	12.9	
42.5	62	540	5.8					132	160	21	6.6	5430	12.3	
45.5	67	449	5.9					100	41	25	6.61	3430	12	
51.5	66	515	5.7					139	55	21	6.2	3700	12	

Table C-7. Standard Chemical and Atomic Absorption Analysis of Core 13 (Mid-channel, St. Joe River, 7.6m Water-depth).

Depth cm	% Water Content	pH	Eh	Total P	NH_3-N	Org. N	Total Org. C	Zn	Mn	Mg	Pb	Fe	Cu	Cd
0-5	85	5.6	245					63.0	110.4	392.0	12.0	3720	10.4	6.00
5-10	80	6.1	170					51.0	109.2	334.8	9.04	3600	9.08	0.80
10-15	64	5.9	185					10.8	102.4	444.8	8.50	3600	9.28	0.16
15-20	53	5.6	240					15.2	104.4	244.8	10.16	3440	10.28	0.28
20-25	51	6.2	175					11.2	97.2	224.0	4.92	2640	6.40	0.20
25-30	56	5.5	230					10.4	42.0	192.8	4.76	1784	6.72	0.06
30-35	51	5.5	240					8.8	60.0	196.0	4.20	2520	12.60	0.057
35-43	57	5.9	270					14.0	98.0	204.0	6.56	3720	16.08	0.25

Table C-8. Standard Chemical and Atomic Absorption Analysis of Core 14 (.4km off Conkling Park, 36.6m Water-depth).

Depth cm	% Water Content	pH	Eh	Total P	NH_3-N	Org. N	Total Org. C	Zn	Mn	Cr	Ni
2.5	82	7.0	100	4000	10	27,000					
6.5	54	6.85	164	2500	15	24,500					
12.5	62	6.6	274	2510	21	17,000					
17.0	73	6.3	208	1750	24.4	13,000		91	320	95	32
22.5	69	6.4	155	1550	35	9,500			330	35	34
26	67	6.45	201	1975	35.9	7,600		157	350	125	30
32.5	65	6.2	199	2800	36.1	7,533		115	320	100	27
36.5	63	6.3	171	3520	36.2	7,517		141	335	135	24.2
42.5	67	6.4	181	3480		7,513		116	325	93	21.7
45.5	68	6.65	185	3516		7,515		116	310	91	22.8
52.5	64		180	3700				119			

Table C-9. Standard Chemical, Total Carbon and Atomic Absorption Analysis of Core A (.215km off West Shore, Plummer Creek Delta, 3m Water-depth).

depth cm	% Water Content	pH	Eh	Total-P	NO_3	Total Organic-C	Cd	Cu	Cr	Mn	Ni	Pb	Zn
0-2				1600		11,900		19	44	284	24.4		81.8
2-4				4013		7,800		28.6	41.8	79.8	31.8		76
4-6						15,400		22.8	72.4	380	33.6		79
6-8								20	63.6	698	27.6		64
8-12						22,500		21	84.8	348	31.8		50
12-14				2533				19	46.4	728	24.4		94
14-16						63,600		22.8	96	728	43.4		70
16-18				3313				17	44	376	41.66		39.8
18-20						18,200		19.7	56.6	470	27.2		50
20-22													
22-24						12,900							
24-26													
26-28						7,200							
28-30						7.200							

Table C-10. Standard Chemical and Atomic Absorption Analysis of Core B (Eastern area of Chatcolet Lake, 3m Water-depth).

depth cm	% Water Content	pH	Eh	Total-P	NO_3	Total Organic-C	Cd	Cu	Cr	Mn	Ni	Pb	Zn
0-2	62	6.3	650	3133	19			25.6	70.4	338	34		84
6-8	57	6.6	720	2367	13.5			22.4	64.8	298	30		78
12-14	52	6.4	720	2333	10.9			18	54.6	188	22.6		44
18-20	49	6.6	735	1533	9.0			18	64.82	181.4	22		48
24-26	53	6.6	730	2367	9.0			21.8	64	390	26		60
30-32	54	6.7	740	3233	9.0			21.8	61.2	310	30		60
36-38	58	6.7	730	3400	7.5			20.2	61.2	320	23.8		60
42-44	62	6.65	735	2633	6.2			20	54.6	198	22.6		70
48-50	76	6.5	720	2400	6.2			14	34.2	129.6	21		42
50-52	76	6.5	670	1233				17	44	133.2	23.8		44

Table C-11. Standard Chemical and Atomic Absorption Analysis of Core C (Mouth of St. Joe River, 7.6m Water-depth).

depth cm	% Water Content	pH	Eh	Total-P	NO_3	Total Organic-C	Cd	Cu	Cr	Mn	Ni	Pb	Zn
0-2	50	6.5	660	2833	3.5			26.18	76.4	282	32		364
6-8	48	6.9	800	2000	12			26.6	72.6	306	30.4	69	72
12-14	54	6.9	770	2000	19.5			29	86.2	332	30.4		98
18-20	51	6.8	800	2540	18			30	81.6	332	26.8		84
24-26	53	6.9	810	2360	12			31.6	87.4	320	32		82
30-32	51	6.7	790	1840	12			27	74.4	301	30.4		104
36-38	57	6.7	860	2733	12.2			24.6	64	282	27		264
42-44	54	6.7	800	1780	10			26.8	72.6	204	32		70
48-50	44	6.9	780					27.4	66.4	262	28.1		64
53-54	44	6.8	790	2000	9.5			31	86	298	32.6		68
60-62	46	6.8	800	2000	9.5			31.6	81.6	282	36.16		67.8
66-68	42	6.8	790	1800	9.5			27.8	76.2	290	32.6		68.6

Table C-12. Standard Chemical and Atomic Absorption Analysis of Core D (1.21km from Mouth of Lake Creek, 7.6m Water-depth).

depth cm	% Water Content	pH	Eh	Total-P	NO_3	Total Organic-C	Cd	Cu	Cr	Mn	Ni	Pb	Zn
	73	6.5	690	2087	21			22.2	91.2	310	30.6		98
	73	6.2	660	2600	25			36.6	41.4		34.6		162
	72	6.25	610	2400	24			32	114.2	356	30.6		108
	71			2353	23			22	87	310	26.8		138
	67			2580	23			33.8	116	340	24.6		107
	70			2333	22			22	85.2	318	22.6		109
								22	87	310	22.6		119

Table C-13. Standard Chemical, Total Carbon and Atomic Absorption Analysis of Core E (3.2km from Mouth of Lake Creek, 10 m Water-depth).

depth cm	% Water Content	pH	Eh	Total-P	NO_3	Total Organic-C	Cd	Cu	Cr	Mn	Ni	Pb	Zn
0-1	68	7	710	3267	21			162	162	6080	58	2260	2700
2-3	63	7	740					20	119	13380	38.1	444	376
4-5	62	7.2	830	3267	30			146	164.6	5380	48.3	5040	3000
8-9	66	6.8	900	2633	13.5			146	180	5740	48.3	5480	3440
12-13	62	6.5	760	4167	5			236	179.4	5740	48.3	13400	4480
19-20	61	6.7	730	4933	5			28.6	127.8	1770		504	338
24-25	65	6.3	780	4733	5			36	142.6	1638	50	682	486
32-33	65	6.4	760	4800	9.5			28.6	127.8	1110	45	222	224
34-35	64	6.5	730					28	131.6	1028	52	168.6	174
39-40	57	6.4	690	4833	6.5			27	113	938	36.2	64.4	300
44-45	54	6.3	680	4700	5.8			24.4	111.8	886	36.6	104	170
48-49	53	6.5	720	4700	9			24.56	133.8		50.4		
50-51	55	6.3	670	3567	8			28.8	127.8	886	42.4	69.6	146

Table C-14. Standard Chemical, Total Carbon and Atomic Analysis of Core G (1.8km from Redford Creek, 8m Water-depth).

depth cm	% Water Content	pH	Eh	Total-P	NO_3	Total Organic-C	Cd	Cu	Cr	Mn	Ni	Pb	Zn
0-2	65	7	740	3167	7.8	11,200		41.6	100	3220	24.5	844	
4-6						11,600		66	113.4	3400	26.72	782	
8-10	29	6.9	745	2567	6.2	10,900		68.8	124.8	3140	26.72	2300	
12-14	31	7	731	2767	6.2	17,200		48.2	113.4	1584	26.72	2302	
16-18	31	6.4	750	3533	5.3	17,600		18	84	794	22.6	3960	240
20-22	31	6.45	735			17,000		18.2	84	730	22.52	238	124
24-26	30	6.4	730	3433	3.2	15,900		22.6	80.6	624	24.6	164.8	252
28-30	30	6.5	715	3500	2.4	15.200		18.2	77.9	502	22.52	164.6	185
32-34	32	6.35	685			14,800		20	92.4	498	30	64	146
36-38	33	6.2	690	3333	3.3	14,600		15	64	396	27	46	104
40-42	31	6.4	691	2833	6	16,100		19	84.26	410	27.9		101
44-46	35	6.4	695	3833	5.5	15,100		17.6	72.4	429	22.9		80.2
48-50	28	6.3	685	3767	<1	14,300		17.4	76.3	420	22.52		130.4
52-54	28	6.4	700		4	16,100		26	80.6	396	30.8		86.6

Table C-15. Standard Chemical and Atomic Absorption Analysis of Core H (1.3km from Tributary Creek, 8m Water-depth).

depth cm	% Water Content	pH	Eh	Total-P	NO_3	Total Organic-C	Cd	Cu	Cr	Mn	Ni	Pb	Zn
0-3	45	7.15	720	3167	6.3			142.8	386.6		50	3260	5240
5-7	51	6.9	740	2433	5.3			170.4	177.8		43.6	5680	3430
7-11	52	7.0	745	1733	5.3			141.6	784		46.4	6860	4100
13-15	53	6.9	780	3533	6.5			238	179.4		45	13680	5200
17-19	67	6.4	665	4400				35.8	126.6		42		1480
21-23	64	6.7	670	5100	6.4			220	119.8	868	31.6	148	218
25-27	64	6.4	690	4067	6.4			33.8	134.9	960	36.4	231.8	290
29-31	67	6.7	690	4600	6.4			24.2	131.6	718	43.6	149	190
33-35	65	6.6	700	4366	5.9			20.4	113	678	42	120.8	170
37-39	65	6.5	750	4767	5.9			22.2	113	612	40	49	138
41-43	64	6.7	800	4100	5.2			24.2	134.9	620	40	43.6	192
43-45	63	6.5	770		12			20.8	113	658	39		188

Table C-16. Standard Chemical, Total Carbon and Atomic Absorption Analysis of Core I (.4km from mouth of Carlin Creek, 7m Water-depth).

depth cm	% Water Content	pH	Eh	Total-P	NO_3	Total Organic-C	Cd	Cu	Cr	Mn	Ni	Pb	Zn
0-2	30	5.4	520	1400	22.5			51.4	44.2	356	31.6	1580	10380
6-8	39	6	570	800	10			14.2	21.4	79.8	26.8		59.6
12-14	60	6.3	650	900	12			33.6	52	140	28.8		61
18-20	58	6.2	715		12			30	34.4	128	34.5		48
24-26	57	6	725	833	12			29.6	38	124	27.9		47.8
30-32	60	6.2	670	900	12			29.5	34.1	123	34.5		50
36-38	65	6.2	650	633	12.5			27.8	34	107	10		59
40-42	64	6	650		18			30	42.6	108	12.2		50

Table C-17. Standard Chemical and Atomic Absorption Analysis of Core J (1km Out From Mouth of Mica Creek, 13m Water-depth).

depth cm	% Water Content	pH	Eh	Total-P	NO_3	Total Organic-C	Cd	Cu	Cr	Mn	Ni	Pb	Zn
0-2	67	7.1	770		11			100.8	131.4	3740	45	8420	4200
2-3	63	7.15	780	2633	11.2				161.2	4900	40.4	5000	3500
4-5	64	6.85	820	3500	8			104.4	172	5090	41.86	7200	3490
7-8	63	6.4	780	2433	6			115	127		36.8	1480	4200
10-11	53	6.7	710	3433	6			34.6	68	1125	30.6	510	4796
14-15	31	5.7	660					18.8	14	220	10.8	0	36

Table C-18. Standard Chemical, Total Carbon and Atomic Absorption Analysis of Core K (Outlet to the Spokane River, 12m Water-depth).

depth cm	% Water Content	pH	Eh	Total-P	NO_3	Total Organic-C	Cd	Cu	Cr	Mn	Ni	Pb	Zn
								105.4	164.8	4160	41.6	5000	4720
								32	131.2	1479	40	1718	1440
								27.8	100	922	34.2	446	370
								23	100.5	630	35.6		70
								25.2	118.6	726	41.6	248	240
								25.8	115.6	600	40.4	165.2	240
								25.18	119.6	560	41.6	125.6	162
								20.6	100	500	40.8	64.8	165
								21	113.4	530	40.8	72.8	120
								21.5	101	450	41.6	78	119
								23.8	113.4	460	43.4	44.2	121

Table C-19. Standard Chemical and Atomic Absorption Analysis of Core L (Bennett Bay, .14km South of U. S. I-90, 9m Water-depth).

depth cm	% Water Content	pH	Eh	Total-P	NO_3	Total Organic-C	Cd	Cu	Cr	Mn	Ni	Pb	Zn
0-3	60	6.7	781	3033	20			30.2	113.4	1190	41.6	1140	3100
7-9	60	6.9	800	2887	6			22.2	100	892	33.6	60	70
13-15	65	6.7	745	3067	5.8			27	96.4	614	38	170.4	220
19-21	64	6.9	780	3333	3			22	88.4	416	38	46.2	99
25-27	64	6.8	720	2166	4			23	88.4	559	33.6	238	240
31-33	64	6.65	740	2900	10			23.4	81.4	478	31.8	133.6	132
37-39	64	6.9	740	3000	10			21.8	76.8	428	31.86		84
43-45	64	6.9	730	3033	10			24.4	96	414	40.4		106
49-51	68	6.8	760	4100	10			66.9	139.8	2840	41.6	245	

Table D-1. Spokane River Quality Data
(expressed as mg/1)

Date Location	River Mile	NO_3-N	NH_3-N	K_j-N	PO_4-P	Total PO_4-P	SO_4	BOD	COD	Cu	Zn	Fe	Mn	Cl
October 21, 1972														
Lake Outlet	110	.05			.000		11.0	.5	3.7					
Ross Point	105	.035			.02		12.3							
Post Falls	102	.015			.007		11.4							
Harvard Road	92	.00			.02		14.2							
Upriver Dam	81	.075			.015		9.3							
Upriver Drive	77													
Gonzaga	74													
November 9, 1972														
Lake Outlet	110	.010	.018	.00	.006	.038	10.7	1.3		.0019	.185	.0026		1.5
Ross Point	105	.025	.045	.00	.032	.112	15.1	1.3		.0014	.189	.0019		1.5
Post Falls	102	.010	.005	1.96	.013	.088	14.1	1.2		.0011	.183	.0027		1.0
Harvard Road	92	.015	.050	.17	.022	.073	11.3	1.7		.0007	.166	.0022		1.0
Upriver Dam	81	.140	.190	.34	.021	.077	9.6	1.8		.001	.155	.0012		1.0
Upriver Drive	77	.225	.035	.06	.018	.088	10.5	.9						1.5
Gonzaga	74	.315	.100	.09	.017	.101	12.0	1.3		.0008	.126	.0008		1.5
November 22, 1972														
Lake Outlet	110	.060	.00	.17	.007	.045	10.9	2.0	5.6	.0005	.202	.0036		.03
Ross Point	105	.030	.00	.17	.012	.100	10.6	1.8	8.0	.0003	.208	.0028		.5
Post Falls	102	.025	.00	.20	.012	.098	12.0	1.5	8.4	.0003	.220	.0027		.5
Harvard Road	92	.025	.00	.17	.010	.080	10.8	1.6	9.2	.0003	.205	.0027		.5
Upriver Dam	81	.21	.00	.17	.011	.090	10.8	1.8	11.2	.0006	.174	.003		.5
Upriver Drive	77	.37	.00	.17	.013	.085	10.9	2.0	14.2	.0008	.127	.002		.5
Gonzaga	74	.33	.00	.22	.014	.085	10.8	1.9	11.2	.0005	.140	.0026		1.0

Table D-1 (Continued)

Date Location	River Mile	NO_3-N	NH_3-N	K_j-N	PO_4-P	Total PO_4-P	SO_4	BOD	COD	Cu	Zn	Fe	Mn	Cl
January 4, 1973														
Lake Outlet	110	.025	.08	.12	.015	.095	5.2	1.3	4.0	.0009	.225	.0048		
Ross Point	105	.020	.08	.15	.025	.125	5.5	1.7	4.8	.0007	.215	.005		
Post Falls	102	.020	.03	.15	.020	.090	5.0	1.3	4.8	.0008	.225	.0035		
Harvard Road	92	.020	.06	.13	.020	.120	5.9	1.8	4.4	.0005	.225	.0032		
Upriver Dam	81	.053	.09	.17	.025	.120	5.2	1.3	2.8	.0005	.215	.0022		
Upriver Drive	77	.113	.03	.15	.025	.265	5.9	1.3	4.0	.0006	.21	.0024		
Gonzaga	74	.113	.08	.17	.030	.130	5.9	1.8	5.6	.0006	.21	.0035		
February 2, 1973														
Lake Outlet	110	.055	.030	.11	.008	.017	10.8	1.6	5.5	.0008	.24	6		
Ross Point	105	.095	.030	.17	.008	.020	12.0	2.2	4.6	.001	.24	6		
Post Falls	102	.073	.042	.11	.007	.020	11.1	1.5	3.6	.0008	.24	3.5		
Harvard Road	92	.070	.025	.11	.007	.025	10.8	1.6	5.9	.001	.24	6		
Upriver Dam	81	.060	.070	.28	.010	.022	10.9	2.2	4.6	.0005	.23	2		
Upriver Drive	77	.075	.040	.28	.007	.020	11.8	1.5	5.0	.0005	.23	3		
Gonzaga	74	.076	.042	.22	.008	.022	12.4	2.1	8.2	.0007	.22	5		
March 3, 1973														
Lake Outlet	110	.030	.10	.112	.070	.103	10.2	1.8	6.38		.26			
Ross Point	105	.025	.05	.280	.078	.105	10.2	2.2	8.21		.27			
Post Falls	102	.015	.11	.112	.078	.115	10.2	1.8	5.47		.27			
Harvard Road	92	.030	.25	.168	.063	.110	10.2	2.0	3.19		.27			
Upriver Dam	81	.065	.07	.224	.065	.093	10.2	1.9	5.02		.27			
Upriver Drive	77	.160	.09	.112	.06]	.093	10.8	1.7	3.19		.22			
Gonzaga	74	.155	.11	.196	.015	.088	10.8	2.6	6.38		.235			

Table D-1 (Continued)

Date Location	River Mile	NO_3-N	NH_3-N	K_j-N	PO_4-P	Total PO_4-P	SO_4	BOD	COD	Cu	Zn	Fe	Mn	Cl
April 6, 1973														
Lake Outlet	110	.035			.047	.057	10.5	1.9	5.7	.0009	.250	.014		
Ross Point	105	.030			.058	.075	10.5	2.0	7.0	.0005	.252	.012		
Post Falls	102	.125			.055	.080	11.2	2.0	8.4	.0009	.285	.012		
Harvard Road	92	.045			.055	.062	11.2	1.7	7.0	.0012	.273			
Upriver Dam	81	.050			.067	.07]	10.0	1.7	6.2	.0011	.267	.011		
Upriver Drive	77	.085			.053	.063	11.5	2.1	6.2	.0008	.250	.014		
Gonzaga	74	.080			.05]	.060	11.0	1.6	5.3	.0025	.236	.011		
May 8, 1973														
Lake Outlet	110	.04	.03	.118	.012	.078	12.6	2.2	10.4	.0005	.219	≃.040		
Ross Point	105	.03	.03	.11	.017	.097	12.4	2.4	10.0	.0003	.266	.028		
Post Falls	102	.04	.02	.11	.012	.093	12.6	1.9	10.0	.0007	.273	.033		
Harvard Road	92	.03	.03	.088	.012	.095	12.6	1.7	9.1	.0006	.270	.030		
Upriver Dam	81	.04	.04	.092	.012	.088	12.8	1.6	7.7	.0006	.276	.023		
Upriver Drive	77	.75	.04	.094	.012	.085	13.0	1.7	7.4	.0005	.258	.029		
Gonzaga	74	.75	.03	.112	.012	.103	12.8	2.4	34.4	.0005	.250	.028		
June 4, 1973														
Lake Outlet	110	.015	.045	.099	.010	.042	11.2			.001		.0092		
Ross Point	105	.015	.055	.095	.012	.088	11.8			.0008		.0075		
Post Falls	102	.010	.025	.104	.008	.083	11.8			.0005		.0088		
Harvard Road	92	.025	.045	.099	.015	.067	11.6			.0007		.006		
Upriver Dam	81	.025	.075	.119	.008	.048	11.8			.0005		.0064		
Upriver Drive	77	.070	.045	.092	.012	.097	12.4			.0009		.0072		
Gonzaga	74	.070	.045	.117	.012	.062	12.4			.0007		.006		

Table D-1 (Continued)

Date Location	River Mile	NO_3-N	NH_3-N	K_j-N	PO_4-P	Total PO_4-P	SO_4	BOD	COD	Cu	Zn	Fe	Mn	Cl
July 6, 1973														
Lake Outlet	110	.035	.04	.26	.006	.057	10.6		6.3					
Ross Point	105	.047	.09	.27	.008	.083	11.2		5.8					
Post Falls	102	.034	.09	.28	.006	.091	10.6		8.5					
Harvard Road	92	.038	.04	.23	.006	.067	12.2		11.2					
Upriver Dam	81	.125	.06	.19	.010	.061	10.8		14.4					
Upriver Drive	77	.270	.04	.20	.006	.061	12.9		9.4					
Gonzaga	74	.411	.09	.32	.015	.092	13.0		9.9					
August 1, 1973														
Lake Outlet	110	.00	.02	.18	.005	.088	10.0	.9	4.1					
Ross Point	105	.00	.03	.28	.088	.151	11.9	2.2	4.5					
Post Falls	102	.00	.03	.31	.04	.095	11.3	1.3	6.6					
Harvard Road	92	.016	.04	.27	.035	.089	12.8	1.5	6.6					
Upriver Dam	81	.20	.03	.14	.02	.099	11.2	2.3	4.9					
Upriver Drive	77	.53	.015	.21	.01	.067	12.2	1.3	2.9					
Gonzaga	74	.56	.01	.11	.01	.063	12.1	1.4						
August 16, 1973														
Lake Outlet	110	<.01	.015			.028	14.4	.5						
Ross Point	105	<.01	.02		.025	.229	13.3	.8						
Post Falls	102	<.01	.02		.164	.181	14.6	1.2						
Harvard Road	92	<.01	.03		.103	.172	18.1	1.1						
Upriver Dam	81	.35	.05			.191	15.2	.8						
Upriver Drive	77	.69	.04			.067	14.9	.9						
Gonzaga	74	.71	.07		.030	.073	18.8	.6						

Table D-1 (Continued)

Date Location	River Mile	NO_3-N	NH_3-N	K_j-N	PO_4-P	Total PO_4-P	SO_4	BOD	COD	Cu	Zn	Fe	Mn	Cl
<u>September 7, 1973</u>														
Lake Outlet	110		.02	.12	.01	.04								
Ross Point	105		.01	.13	.01	.05								
Post Falls	102		.01	.18	.055	.10								
Harvard Road	92		.04	.22	.06	.08								
Upriver Dam	81		.04	.22	.05	.11								
Upriver Drive	77		.04	.22	.05	.09								
Gonzaga	74		.08	.34	.02	.15								
<u>October 16, 1973</u>														
Lake Outlet	110	<.002			.003		9.8	.9						.75
Ross Point	105	<.002			.022	.05	9.6	.8						1.0
Post Falls	102	<.002			.053	.10	8.8	.8						1.0
Harvard Road	92	<.002	.004		.030	.06	9.8	1.4						1.0
Upriver Dam	81	<.002	.015		.007	.08	10.4	2.0						1.0
Upriver Drive	77	.080	.008		.009	.05	12.8	1.5						1.0
Gonzaga	74	.093	.005		.007	.05	10.4	1.4						1.0
<u>November 14, 1973</u>														
Lake Outlet	110	.039	≈.20		.01	.12	10.2	.00						
Ross Point	105	.043	.16		.05	.14	9.8	.7						
Post Falls	102	.043	.15		.04	.15	9.4	.4						
Harvard Road	92													
Upriver Dam	81													
Upriver Drive	77													
Gonzaga	74	.192	.03		.035	.15	11.4	1.5						

Table D-1 (Continued)

Date Location	River Mile	NO_3-N	NH_3-N	K_j-N	PO_4-P	Total PO_4-P	SO_4	BOD	COD	Cu	Zn	Fe	Mn	Cl
December 18, 1973														
Lake Outlet	110	.083	.004		.012	.10	9.2	.6						
Ross Point	105	.081	.006		.012	.08	9.0	.8						
Post Falls	102	.084	.006		.008	.07	9.6	.8						
Harvard Road	92	.086	.006		.008	.11	8.4	1.6						
Upriver Dam	81	.091	.01		.004	.10	9.6	1.3						
Upriver Drive	77	.093	.01		.006	.12	9.0	1.8						
Gonzaga	74	.095	.01		.007	.12	10.4	1.2						
January 23, 1974														
Lake Outlet	110	.140	.03		.029	.10		.9	5.0					
Ross Point	105	.181	.035		.048	.05		.8	4.8					
Post Falls	102	.155	.038		.034	.06		.2	4.8					
Harvard Road	92	.148	.025		.035	.08		1.1	4.9					
Upriver Dam	81	.182	.040		.050	.05		1.0	5.0					
Upriver Drive	77	.152	.027		.026	.05		1.0	4.8					
Gonzaga	74	.180	.025		.050	.04		.8	5.0					
Plantes Ferry	84	.175	.030		.027	.05		1.5	4.9					
February 19, 1974														
Lake Outlet	110	.045		.23	.024	.12	9.0	.5						
Ross Point	105	.035		.26	.021	.17	9.0	.6						
Post Falls	102	.040		.26	.025	.16	9.0	1.0						
Harvard Road	92	.033		.21	.024	≃.10	9.0	.9						
Upriver Dam	81	.044		.23	.023	.10	9.0	.8						
Upriver Drive	77	.043		≃.20	.021	.10	9.0	1.5						
Gonzaga	74	.042		≃.20	.024	.11	9.0	1.1						
Plantes Ferry	84	.042		.19	.023	.10	9.0	.1						

Table D-1 (Continued)

Date Location	River Mile	NO_3-N	NH_3-N	K_jN	PO_4-P	Total PO_4-P	SO_4	BOD	COD	Cu	Zn	Fe	Mn	Cl
March 15, 1974														
Lake Outlet	110	.040					9.0	.8						
Ross Point	105	.034					10.0	.4						
Post Falls	102	.041					9.0	.6						
Harvard Road	92	.045					10.0	.6						
Upriver Dam	81	.048					12.0	.3						
Upriver Drive	77	.031					10.0	.7						
Gonzaga	74	.032					10.0	1.0						
Plantes Ferry	84	.033					10.0	.7						
April 2, 1974														
Lake Outlet	110							.8						
Ross Point	105							.5						
Post Falls	102							.5						
Harvard Road	92							.7						
Upriver Dam	81							.9						
Upriver Drive	77							.5						
Gonzaga	74							1.4						
Plantes Ferry	84							.6						

Table D-1 (Continued)

Date Location	River Mile	Temp. C	pH	O_2 mg/l	O_2 % Sat.	CO_2 mg/l	CO_3 mg/l	HCO_3 mg/l	Conductivity Micro-mhos at 25 C
October 21, 1972									
Lake Outlet	110								
Ross Point	105								
Post Falls	102								
Harvard Road	92								
Upriver Dam	81								
Upriver Drive	77								
Gonzaga	74								
November 9, 1972									
Lake Outlet	110								
Ross Point	105								
Post Falls	102								
Harvard Road	92								
Upriver Dam	81								
Upriver Driver	77								
Gonzaga	74								
November 22, 1972									
Lake Outlet	110	7.9		9.8	88	1		19	59
Ross Point	105	7.9		9.5	86	1		21	59
Post Falls	102	7.9		10.5	95	2		21	60
Harvard Road	92	7.0		10.5	93	2		21	60
Upriver Dam	81	7.0		10.1	89	3		37	65
Upriver Drive	77	7.3		7.3	65	2		50	78
Gonzaga	74	7.3		7.1	63	2		48	70

Table D-1 (Continued)

Date Location	River Mile	Temp. C	pH	O_2 mg/1	O_2 % Sat.	CO_2 mg/1	CO_3 mg/1	HCO_3 mg/1	Conductivity Micro-mhos at 25 C
January 4, 1973									
Lake Outlet	110	2.2		11.7	92				<50
Ross Point	105	2.0		11.6	91				51
Post Falls	102	3.0		11.9	95				51
Harvard Road	92	2.5		12.6	101				<50
Upriver Dam	81	2.0		12.3	94				52
Upriver Drive	77	2.3		12.4	98				85
Gonzaga	74	4.5		12.4	102				88
February 2, 1973									
Lake Outlet	110	≃4.0		12.2	101	3			45.8
Ross Point	105	≃4.0		12.2	101	3			45.8
Post Falls	102	≃4.0		12.1	100	3			46.8
Harvard Road	92	≃4.0		12.0	99	2			46.8
Upriver Dam	81	≃4.0		12.8	106	3			53.2
Upriver Drive	77	≃4.0		12.9	107	3			58.5
Gonzaga	74	≃4.0		12.9	107	4			58.5
March 3, 1973									
Lake Outlet	110	4.2		12.8	106	4			55.7
Ross Point	105	4.5		12.8	106	5			55.7
Post Falls	102	4.0		12.7	105	5			55.7
Harvard Road	92	4.0		12.9	106	3			55.7
Upriver Dam	81	4.0		12.3	101	5			73.1
Upriver Drive	77	4.8		12.4	103	4			88.6
Gonzaga	74	4.8		12.1	103	5			88.6

Table D-1 (Continued)

Date Location	River Mile	Temp. C	pH	O_2 mg/l	O_2 % Sat.	CO_2 mg/l	CO_3 mg/l	HCO_3 mg/l	Conductivity Micro-mhos at 25 C
April 6, 1973									
Lake Outlet	110	7.9		12.4	113				
Ross Point	105	7.9		12.4	113				
Post Falls	102	7.9		12.7	115				
Harvard Road	92	7.9		12.3	112				
Upriver Dam	81	7.9		12.2	111				
Upriver Drive	77	7.9		12.1	110				
Gonzaga	74	7.9		11.9	108				
May 8, 1973									
Lake Outlet	110	10		11.1	110	5			60
Ross Point	105	10		11.2	112	6			58
Post Falls	102	10		11.2	112	5			62
Harvard Road	92	11		10.7	103	5			61
Upriver Dam	81	10		10.5	104	5			62
Upriver Drive	77	10		10.7	105	5			75
Gonzaga	74	10		10.6	104	5			75
June 4, 1973									
Lake Outlet	110	14.5		10.2	107	5			<50
Ross Point	105	14.5		9.9	104	5			60
Post Falls	102	13		9.9	101	5			60
Harvard Road	92	13		10.2	104	4			60
Upriver Dam	81	13		9.6	98	4			65
Upriver Drive	77	13		9.8	100	5			85
Gonzaga	74	13		9.6	98	5			85

Table D-1 (Continued)

Date Location	River Mile	Temp. C	pH	O_2 mg/l	O_2 % Sat.	CO_2 mg/l	CO_3 mg/l	HCO_3 mg/l	Conductivity Micro- mhos at 25 C
<u>July 6, 1973</u>									
Lake Outlet	110	20.5	6.8	9.4	111	3			<50
Ross Point	105	21	6.7	9.6	116	2			<50
Post Falls	102	21		9	108	3			50
Harvard Road	92	21	7.5	9	108	.05			52
Upriver Dam	81	21		9	145	0			80
Upriver Drive	77	18		12	131	3			130
Gonzaga	74	18	6.85	11.5	131	2			130
<u>August 1, 1973</u>									
Lake Outlet	110	25	7.4	8.0	103	2			53
Ross Point	105	27	7.1	8.5	113	2			56
Post Falls	102	27	7.3	8.6	115	2			56
Harvard Road	92	23	8.2	8.2	102	2			56
Upriver Dam	81	23	8.7	10.5	130	0			138
Upriver Drive	77	18.5	8.5	11.0	125	0			195
Gonzaga	74	18	6.9	9.0	102	2			195
<u>August 16, 1973</u>									
Lake Outlet	110	23	7.4			.2			60
Ross Point	105	25	7.1			.2			60
Post Falls	102	25	7.3			.2			65
Harvard Road	92	24	8.2						70
Upriver Dam	81	21	8.7						140
Upriver Drive	77	17	8.5						200
Gonzaga	74	15	6.9			.5			215

Table D-1 (Continued)

Date Location	River Mile	Temp. C	pH	O_2 mg/1	O_2 % Sat.	CO_2 mg/1	CO_3 mg/1	HCO_3 mg/1	Conductivity Micro-mhos at 25 C
September 7, 1973									
Lake Outlet	110	18		9.4	117				
Ross Point	105	18		8.5	109				
Post Falls	102	18		8.9	114				
Harvard Road	92	17		9	114				
Upriver Dam	81	17		10.1	122				
Upriver Drive	77	17		10.2	115				
Gonzaga	74	17		10.4	111				
October 16, 1973									
Lake Outlet	110		7.2			2			58
Ross Point	105		7.2			1			58
Post Falls	102		7.3			1			58
Harvard Road	92		7.2			1			58
Upriver Dam	81		7.5			2			74
Upriver Drive	77		7.8			2			94
Gonzaga	74		7.8			2			96
November 14, 1973									
Lake Outlet	110								
Ross Point	105								
Post Falls	102								
Harvard Road	92								
Upriver Dam	81								
Upriver Drive	77								
Gonzaga	74								

Table D-1 (Continued)

Date Location	River Mile	Temp. C	pH	O_2 mg/l	O_2 % Sat.	CO_2 mg/l	CO_3 mg/l	HCO_3 mg/l	Conductivity Micro-mhos at 25 C
December 18, 1973									
Lake Outlet	110								
Ross Point	105								
Post Falls	102								
Harvard Road	92								
Upriver Dam	81								
Upriver Drive	77								
Gonzaga	74								
January 23, 1974									
Lake Outlet	110	3	6.3	11.7	94	5.0		20	39
Ross Point	105	3	6.5	11.6	94	4.0		20	40
Post Falls	102	3	6.5	11.7	94			21	40
Harvard Road	92	3	6.4	14.1	113	6.0		20	40
Upriver Dam	81	3	6.8	14.1	113	5.0		27	40
Upriver Drive	77	3	7.4	14.3	114	6.0		25	44
Gonzaga	74	3	7.0	14.1	113	4.0		29	46
Plantes Ferry	84	4	6.8	14.1	117	4.0		33	44
February 19, 1974									
Lake Outlet	110	4	6.9	10.5	87	3.0		20	53
Ross Point	105	4	6.5	11.5	95	3.0		19	55
Post Falls	102	4		11.2	93	4.0		18	54
Harvard Road	92	4		11.1	92	3.0		17	53
Upriver Dam	81	4		11.8	98	2.0		21	58
Upriver Drive	77	4		11.3	93	3.0		23	60
Gonzaga	74	4		12.0	99	3.0		24	60
Plantes Ferry	84	4		11.4	94	2.0		24	60

Table D-1 (Continued)

Date Location	River Mile	Temp. C	pH	O_2 mg/l	O_2 % Sat.	CO_2 mg/l	CO_3 mg/l	HCO_3 mg/l	Conductivity Micro-mhos at 25 C
March 15, 1974									
Lake Outlet	110	3	6.9	11.9	95	4.0		21	52
Ross Point	105	3	6.9	12.2	98	2.0		25	52
Post Falls	102	4	7.0	12.2	101	3.0		23	58
Harvard Road	92	4	7.1	12.8	106	4.0		28	55
Upriver Dam	81	4	6.8	12.1	100	4.0		31	58
Upriver Drive	77	4	7.6	12.2	101	2.0		31	62
Gonzaga	74	4	7.0	12.3	102	3.0		33	62
Plantes Ferry	84	4	6.9	11.9	98	4.0		34	64
April 2, 1974									
Lake Outlet	110	4	7.2	11.2	93	3.0		18	51.3
Ross Point	105	4	6.8	11.3	93	3.0		16	52.5
Post Falls	102	6	7.0	11.2	90	4.0		20	52.9
Harvard Road	92	4	6.9	10.2	84	2.0		15	50.9
Upriver Dam	81	4	6.9	12.8	106	13.0		6	53.2
Upriver Drive	77	6	6.6	12.5	109	2		19	56.0
Gonzaga	74	6	6.9	12.4	108	3		20	53.7
Plantes Ferry	84	5	7.0	11.2	109	3		18	55.7

Table D-2. Algae Composition of the Spokane River (organisms/ml).

LAKE OUTLET

DIATOMS (BACILLARIOPHYTA)	1/4/73	5/8/73	6/4/73	7/6/73	8/1/73	8/16/73	9/7/73	10/16/73	10/24/73	11/14/73	11/22/73	11/30/73	1/23/74	2/21/74	3/15/74	4/2/74
Achnanthes sp.																
Achnanthes lanceolata																
Amphora sp.																
Asterionella sp.	12	192	165	82				7						55	21	34
Asterionella formosa																
Cocconeis sp.																
Cyclotella sp.		82	14	7						14		7		7		14
Cyclotella ocellata																
Cymbella sp.		14								7				7		
Diatoma sp.		7														
Diatoma circulare																
Diatoma hiemale																
Diatoma vulgare																
Diatomella sp.																
Epithemia sp.																
Eunotia sp.																
Fragilaria sp.		21			27			21		233		62	41	117		
Fragilaria construens																
Fragilaria crotonensis																
Frustulia sp.																
Frustulia rhomboides																
Gomphonema sp.		7														
Hannaea arcus																
Melosira sp.	624	1292	809	150	82	96	34	55	55	220	962	693	225	217	329	206
Melosira italica																
Melosira varians																
Meridion sp.																
Navicula sp.		117	21	21	27									7		
Navicula rhynchocephala																
Nitzchia sp.																
Pinnularia sp.																
Rhizosolenia sp.																
Rhoicosphenia curvata																
Surirella sp.																
Synedra sp.	110	89	55	62		48	10	21	7	21	36	21	14	14	27	
Synedra acus																
Synedra contrasta																
Synedra ulna																
Tabellaria sp.	32	89	14	21		14	42	700	226		48	48	1	14	34	
Tabellaria fenestrata										69						
GREENS (CHLOROPHYTA)																
Ankistrodesmus falcatus	4										8					
Ceratium sp.																
Chlamydomonas sp.																
Closterium sp.																
Coelastrum sp.																
Euglena sp.																
Euastrum sp.																
Gloeocystis sp.				10		213										
Mougeotia sp.																
Pediastrum sp.																
Penium sp.																
Planktosphaeria sp.																
Scenedesmus sp.		7														
Scenedesmus quadricauda																
Selenastrum												1				
Schroederia sp.																
Sphaerocystis sp.																
Staurastrum sp.							6		14							
Trachelomonas sp.																
Ulothrix sp.																
YELLOW-GREENS (CHRYSOPHYTA)																
Tribonema sp.					27		138	7								
BLUE-GREENS (CYANOPHYTA)																
Anabaena sp.																
Aphanizomenon sp.					3073	55			158			144				
Nostoc sp.																
Oscillatoria sp.																

Table D-2. (Continued)

ROSS POINT

DIATOMS (BACILLARIOPHYTA)	1/4/73	4/6/73	5/8/73	6/4/73	7/6/73	8/1/73	8/16/73	9/18/73	10/6/73	10/21/73	11/14/73	11/22/73	11/30/73	1/23/74	2/26/74	4/2/74
Achnanthes sp.																
Achnanthes lanceolata																
Amphora sp.																
Asterionella sp.	57	178		103	14	14								41	21	
Asterionella formosa													21			
Cocconeis sp.																
Cyclotella sp.		14		21	14	27					14					7
Cyclotella ocellata																
Cymbella sp.			62													
Diatoma sp.																
Diatoma circulare																
Diatoma hiemale																
Diatoma vulgare																
Diatomella sp.																
Epithemia sp.																
Eunotia sp.																
Fragilaria sp.			7			1564	117	6	82				7			34
Fragilaria construens																
Fragilaria crotonensis																
Frustulia sp.																
Frustulia rhomboides																
Gomphonema sp.					7											
Hannaea arcus																
Melosira italica	856	1660	1125	856	67	165	60	20	89	184	220	810	885	188	217	226
Melosira varians																
Meridion sp.																
Navicula sp.		21	14		14				7							
Navicula rhynchocephala																
Nitzchia sp.																
Pinnularia sp.																
Rhizosolenia sp.																
Rhoicosphenia curvata																
Surirella sp.					7											
Synedra sp.	50	110	34	34	14		370	96		44	14	64	27	27	41	7
Synedra acus																
Synedra contrasta																
Synedra ulna																
Tabellaria sp.	32	165	14	14	14	41	48	198	521	162	27	48	7	14	21	62
Tabellaria fenestrata													55			
GREENS (CHLOROPHYTA)																
Ankistrodesmus falcatus					48											
Ceratium sp.																
Chlamydomonas sp.																
Closterium sp.																
Coelastrum sp.																
Euglena sp.																
Euastrum sp.																
Gloeocystis sp.																
Mougeotia sp.					7		62									
Pediastrum sp.																
Penium sp.																
Planktosphaeria sp.																
Scenedesmus sp.																
Scenedesmus quadricauda																
Selenastrum																
Schroederia sp.											7					
Sphaerocystis sp.																
Staurastrum sp.							21	6								
Trachelomonas sp.																
Ulothrix sp.																
YELLOW-GREENS (CHRYSOPHYTA)																
Tribonema sp.						206		216			14					
BLUE-GREENS (CYANOPHYTA)																
Anabaena sp.																
Aphanizomenon flos-aquae			19	15		1331			48		96		79	41	25	
Nostoc sp.																
Oscillatoria sp.																

Table D-2. (Continued)

POST FALLS

	1/4/73	4/6/73	5/8/73	6/4/73	7/6/73	8/1/73	8/16/73	9/7/73	9/18/73	10/16/73	10/21/73	11/14/73	11/22/73	11/30/73	1/23/74	2/26/74	3/15/74	4/2/74
DIATOMS (BACILLARIOPHYTA)																		
Achnanthes sp.																		
Achnanthes lanceolata																		
Amphora sp.																		
Asterionella sp.	62	151	158	62	27										7	34	14	7
Asterionella formosa														27				
Cocconeis sp.																		
Cyclotella sp.	34	14	27		14					27						7	21	
Cyclotella ocellata																		
Cymbella sp.																	7	
Diatoma sp.																		
Diatoma circulare																		
Diatoma hiemale																		
Diatoma vulgare														7				
Diatomella sp.																		
Epithemia sp.																		
Eunotia sp.																		
Fragilaria sp.		69	14			1550	1098	8		5							316	
Fragilaria construens																		
Fragilaria crotonensis																		
Frustulia sp.																		
Frustulia rhomboides																		
Gomphonema sp.																		
Hannaea arcus																		
Melosira italica	801	1526	1255	656	189	55	123	120	50	137	160	233	640	748	206	194	295	243
Melosira varians																		
Meridion sp.																		
Navicula sp.		34	7		48							7					151	
Navicula rhynchocephala																		
Nitzchia sp.																		
Pinnularia sp.										14		7					27	
Rhizosolenia sp.																		
Rhoicosphenia curvata																		
Surirella sp.																		
Synedra sp.	96	69	82	62	103		82		30	110		14	20	34	7	7	62	7
Synedra acus								80										
Synedra contrasta																		
Synedra ulna											10							
Tabellaria sp.	34	27	55	55	7		425	52	118	1207			4	21			137	7
Tabellaria fenestrata											78	55						
GREENS (CHLOROPHYTA)																		
Ankistrodesmus falcatus																		
Ceratium sp.																		
Chlamydomonas sp.																		
Closterium sp.																		
Coelastrum sp.																		
Euglena sp.																		
Euastrum sp.																		
Gloeocystis sp.																		
Mougeotia sp.																		
Pediastrum sp.							14											
Penium sp.																		
Planktosphaeria sp.																		
Scenedesmus sp.																		
Scenedesmus quadricauda																		
Selenastrum																		
Schroederia sp.																		
Sphaerocystis sp.																		
Staurastrum sp.							123	8								1		
Trachelomonas sp.																		
Ulothrix sp.							96	14				14						
YELLOW-GREENS (CHRYSOPHYTA)																		
Tribonema sp.														14				
BLUE-GREENS (CYANOPHYTA)																		
Anabaena sp.																		
Aphanizomenon flos-aquae			40	5.3		707						99		196	74	7		66
Nostoc sp.																		
Oscillatoria sp.																		

Table D-2. (Continued)

HARVARD ROAD

DIATOMS (BACILLARIOPHYTA)	1/4/73	4/6/73	5/8/73	6/4/73	7/6/73	8/1/73	8/16/73	9/7/73	9/14/73	9/18/73	10/16/73	10/21/73	11/20/73	11/30/73	1/23/74	2/26/74	3/15/74	4/2/74
Achnanthes sp.																		
Achnanthes lanceolata																		
Amphora sp.																		
Asterionella sp.	55	130	89	165			7	7			7				14	48	7	27
Asterionella formosa														7				
Cocconeis sp.																		
Cyclotella sp.	27	27	7	7														
Cyclotella ocellata																		
Cymbella sp.		14	7			7								14	7			
Diatoma sp.				7														
Diatoma circulare																		
Diatoma hiemale																		
Diatoma vulgare																		
Diatomella sp.																		
Epithemia sp.																		
Eunotia sp.																		
Fragilaria sp.			14			1290	233	34	8		89	10		34				
Fragilaria construens																		
Fragilaria crotonensis																		
Frustulia sp.																		
Frustulia rhomboides																		
Gomphonema sp.														7				
Hannaea arcus																		
Melosira italica	877	1769	1104	816	85	130		69	16	8	82	226	454	672	229	272	288	220
Melosira varians																		
Meridion sp.																		
Navicula sp.	21	34	14		62	14									7	7	7	7
Navicula rhynchocephala																		
Nitzchia sp.														14				
Pinnularia sp.														7				
Rhizosolenia sp.														21				
Surirella sp.																		
Synedra sp.	27	75	41	103	69		213	34	20	20	34	14	28	55	34	14	14	14
Synedra acus																		
Synedra contrasta																		
Synedra ulna																		
Tabellaria sp.	21	55	41	55	7		322	69		58	521	222		14	82			
Tabellaria fenestrata																		
GREENS (CHLOROPHYTA)																		
Ankistrodesmus falcatus									14									
Ceratium sp.																		
Chlamydomonas sp.																		
Closterium sp.																		
Coelastrum sp.																		
Euglena sp.																		
Euastrum sp.									4									
Gloeocystis sp.																		
Mougeotia sp.																		
Pediastrum sp.																		
Penium sp.																		
Planktosphaeria sp.																		
Scenedesmus sp.																		
Scenedesmus quadricauda																		
Selenastrum																		
Schroederia sp.																		
Sphaerocystis sp.																		
Staurastrum sp.						7	55			2	7							
Trachelomonas sp.																		
Ulothrix sp.							34	41										
YELLOW-GREENS (CHRYSOPHYTA)																		
Tribonema sp.						55		357		28				21				
BLUE-GREENS (CYANOPHYTA)																		
Anabaena sp.																		
Aphanizomenon flos-aquae			28			285					41			281	36	4	49	
Nostoc sp.																		
Oscillatoria sp.																		

PLANTES FERRY

Table D-2. (Continued)

DIATOMS (BACILLARIOPHYTA)	8/16/73	9/7/73	9/14/73	9/18/73	11/30/73	1/23/74	2/26/74	3/15/74	4/2/74
Asterionella sp.						21	21	48	14
Asterionella formosa					7				
Cocconeis sp.									
Cyclotella sp.									34
Cymbella sp.		28		6					
Diatoma sp.									
Diatoma vulgare									
Eunotia sp.									
Fragilaria crotonensis	69			4	14			14	
Frustulia sp.									
Gomphonema sp.						7			
Hannaea arcus					7			7	
Melosira italica	7	72	104	14	720	118	176	191	294
Navicula sp.					14	7			
Nitzchia sp.		4			7				
Pinnularia sp.					7				
Rhizosolenia sp.					14				
Surirella sp.							1		1
Synedra sp.	103	110	134	20	55	27	7		7
Tabellaria sp.	89		172	42	48			21	7
Tabellaria fenestrata		174							
GREENS (CHLOROPHYTA)									
Ankistrodesmus falcatus		40							
Chlamydomonas sp.									
Chlorella sp.	10	12		18	6	2			
Dinobryon sp.	34								
Euglena sp.	4								
Gloeocystis sp.	16								
Mougeotia sp.	4								
Planktosphaeria sp.	1	1							
Scenedesmus quadricauda	18	28		16					
Schroederia sp.									
Staurastrum sp.	27	18							
Ulothrix sp.	421			362	27				
YELLOW-GREENS (CHRYSOPHYTA)									
Tribonema	15			8					
BLUE-GREENS (CYANOPHYTA)									
Anabaena sp.	8			12					
Aphanizomenon flos-aquae	16			1.4	144	18		7	
Nostoc sp.									
Oscillatoria sp.	6			4					

Table D-2. (Continued)

UP RIVER DAM

DIATOMS (BACILLARIOPHYTA)	1/4/73	4/6/73	5/8/73	6/4/73	7/6/73	8/1/73	8/16/73	9/7/73	9/18/73	10/16/73	11/22/73	11/30/73	1/23/74	2/26/74	3/15/74	4/2/74
Achnanthes sp.																
Achnanthes lanceolata																
Amphora sp.																
Asterionella sp.	41	254	123	178	27		1				6	7	34	14		27
Asterionella formosa																
Cocconeis sp.																
Cyclotella sp.	14	7		14						7			7			
Cyclotella ocellata																
Cymbella sp.			7				2									
Diatoma sp.				14												
Diatoma circulare																
Diatoma hiemale																
Diatoma vulgare																
Diatomella sp.																
Epithemia sp.																
Eunotia sp.																
Fragilaria sp.			14		14	2017	89015			199	4	34			55	
Fragilaria construens																
Fragilaria crotonensis																
Frustulia sp.																
Frustulia rhomboides																
Gomphonema sp.										75	2	14				
Hannaea arcus																
Melosira italica	1002	1585	838	1052	172	82	4		36	679	534	672	254	244	235	280
Melosira varians																
Meridion sp.																
Navicula sp.	14		14	21	14	27	4			199						
Navicula rhynchocephala																
Nitzchia sp.									14							
Pinnularia sp.										34						
Rhizosolenia sp.												7				
Surirella sp.					7											
Synedra sp.	55	48	55	96	82		5	22	20	151	20	14	34	27	14	14
Synedra acus																
Synedra contrasta																
Synedra ulna																
Tabellaria sp.	55	48	21	75	27		1	114	72	1338	8	27	14	7		
Tabellaria fenestrata																
GREENS (CHLOROPHYTA)																
Ankistrodesmus falcatus								12								
Ceratium sp.																
Chlamydomonas sp.																
Closterium sp.																
Coelastrum sp.																
Euglena sp.																
Euastrum sp.																
Gloeocystis sp.																
Mougeotia sp.																
Pediastrum sp.																
Penium sp.																
Planktosphaeria sp.																
Scenedesmus sp.					14	220	6	10								
Scenedesmus quadricauda																
Selenastrum										96						
Schroederia sp.																
Sphaerocystis sp.																
Staurastrum sp.										14						
Trachelomonas sp.																
Ulothrix sp.							31									14
YELLOW-GREENS (CHRYSOPHYTA)																
Tribonema sp.				10		48			100							
BLUE-GREENS (CYANOPHYTA)																
Anabaena sp.																
Aphanizomenon flos-aquae			14	36		271				13						47
Nostoc sp.																
Oscillatoria sp.																

Table D-2. (Continued)

UP RIVER DRIVE

	4/6/73	5/8/73	6/15/73	7/6/73	8/1/73	8/16/73	9/7/73	9/18/73	10/16/73	11/9/73	11/14/73	11/22/73	11/30/73	1/23/74	2/26/74	3/15/74	4/2/74
DIATOMS (BACILLARIOPHYTA)																	
Achnanthes sp.																	
Achnanthes lanceolata																	
Amphora sp.																	
Asterionella sp.	151	82	123	7											21	21	34
Asterionella formosa																	
Cocconeis sp.													14				
Cyclotella sp.		21	7	7					7				14			14	
Cyclotella ocellata																	
Cymbella sp.														7			
Diatoma sp.		7		7													
Diatoma circulare																	
Diatoma hiemale																	
Diatoma vulgare																	
Diatomella sp.																	
Epithemia sp.																	
Eunotia sp.																	
Fragilaria sp.	14	55			1050	1358	123	26		4	14						
Fragilaria construens																	
Fragilaria crotonensis																	
Frustulia sp.																	
Frustulia rhomboides																	
Gomphonema sp.														7			
Hannaea arcus																	
Melosira italica	1644	938	916	48	34	27	89	84	82	908	82	560	713	187	166	200	342
Melosira varians																	
Meridion sp.																	
Navicula sp.	34	21	7	21	48		7		27				27				
Navicula rhynchocephala																	
Nitzchia sp.					7			24			7						
Pinnularia sp.						7		4			7						
Rhizosolenia sp.													7				
Surirella sp.																	
Synedra sp.	62	62	62	48	7		48	86	21		34	32	34	21	7	14	14
Synedra acus																	
Synedra contrasta																	
Synedra ulna										26							
Tabellaria sp.	5	34	27	14		21	41	86	439	40	21		62	27	7		27
Tabellaria fenestrata																	
GREENS (CHLOROPHYTA)																	
Ankistrodesmus falcatus																	
Ceratium sp.																	
Chlamydomonas sp.																	
Closterium sp.																	
Euglena sp.																	
Euastrum sp.																	
Gloeocystis sp.																	
Mougeotia sp.				8		21											
Pediastrum sp.																	
Penium sp.																	
Planktosphaeria sp.																	
Scenedesmus sp.					69	55											
Scenedesmus quadricauda																	
Selenastrum							55		27								
Schroederia sp.																	
Sphaerocystis sp.																	
Staurastrum sp.					7				7								
Trachelomonas sp.																	
Ulothrix sp.											27		329				
YELLOW-GREENS (CHRYSOPHYTA)																	
Tribonema sp.					137			100			14						
BLUE-GREENS (CYANOPHYTA)																	
Anabaena sp.																	
Aphanizomenon flos-aquae					45				48		87		175	12	19		
Nostoc sp.																	
Oscillatoria sp.																	

Table D-2. (Continued)

GONZAGA

DIATOMA (BACILLARIOPHYTA)	1/4/73	4/6/73	5/8/73	6/4/73	7/27/73	8/1/73	8/16/73	9/7/73	10/16/73	11/14/73	11/22/73	11/30/73	1/23/74	2/26/74	3/15/74	4/2/74
Achnanthes sp.																
Achnanthes lanceolata																
Amphora sp.																
Asterionella sp.		96	69	151	14								21	48	89	55
Asterionella formosa																
Cocconeis sp.																
Cyclotella sp.		21	14	21								55		7	7	7
Cyclotella ocellata																
Cymbella sp.		7	7				21					7				
Diatoma sp.			14													
Diatoma circulare																
Diatoma hiemale																
Diatoma vulgare																
Diatomella sp.																
Epithemia sp.																
Eunotia sp.																
Fragilaria sp.					123	1626	1104		21	14				69	14	
Fragilaria construens																
Fragilaria crotonensis																
Frustulia sp.																
Frustulia rhomboides																
Gomphonema sp.							7		21	7						
Hannaea arcus						34	14	44						7		
Melosira italica	460	1545	1091	760	63	62	62	120	185	110	602	782	180	221	235	328
Melosira varians																
Meridion sp.																
Navicula sp.		62	7		21	21	21		21	7						
Navicula rhynchocephala																
Nitzchia sp.							7	32								
Pinnularia sp.									14			7				
Rhizosolenia sp.												7				
Surirella sp.					1											
Synedra sp.	28	82	69	82	41	7	7	114	55	96	46	48	14	7	14	27
Synedra acus																
Synedra contrasta																
Synedra ulna																
Tabellaria sp.		14	82	21	27				576	41		41	21	7	27	14
Tabellaria fenestrata								102								
GREENS (CHLOROPHYTA)																
Ankistrodesmus falcatus																
Ceratium sp.																
Chlamydomonas sp.																
Closterium sp.																
Coelastrum sp.																
Euglena sp.																
Euastrum sp.																
Gloeocystis sp.																
Mougeotia sp.																
Pediastrum sp.																
Penium sp.																
Planktosphaeria sp.																
Scenedesmus sp.						220	48	12								
Scenedesmus quadricauda																
Selenastrum																
Schroederia sp.																
Sphaerocystis sp.																
Staurastrum sp.						7		2								
Trachelomonas sp.																
Ulothrix sp.							110			274						
YELLOW-GREENS (CHRYSOPHYTA)																
Tribonema sp.										27		21				
BLUE-GREENS (CYANOPHYTA)																
Anabaena sp.																
Aphanizomenon flos-aquae			9			216	7			27		89	29			
Nostoc sp.																
Oscillatoria sp.																

Table D-3. Spokane River Invertebrate Data
Ross Point Station Collected August 9, 1973.

Organism	Number of Organisms No./m^2
Diptera (true flies)	
Chironomidae (midges)	
Prodladius sp.	1434
Glyptotendipes sp.	4304
Total Species	2
Total Organisms	5738
Diversity Index ($\bar{d}$)	.811

Table D-3 (Continued). Harvard Road Station Collected July 31, 1973.

Organism	Number of Organisms No./m^2
Ephemeroptera (mayflies)	
Baetis sp.	58
Trichoptera (caddisflies)	
Hydropsyche sp.	1568
Cheumatopsyche sp.	639
Dicosmoecus sp.	29
Diptera (true flies)	
Chironomidae (midges)	
Procladius sp.	35
Cardiocladius sp.	1500
Polypedilum sp.	1030
Empididae (dance flies)	19
Simuliidae (black flies)	77
Lepidoptera (aquatic moths)	
Parargyractis sp.	10
Turbellaria (flatworms)	
Dugesia sp.	29
Oligochaeta (aquatic worms)	19
Hydracarina (aquatic mites)	164

Total Species	13
Total Organisms	5177
Diversity Index ($\bar{d}$)	2.406

Table D-3 (Continued). Plantes Ferry Station Collected August 1, 1973.

Organism	Number of Organisms No./m^2
Plecoptera (stoneflies)	
Isogenus sp.	29
Sphemeroptera (mayflies)	
Baetis sp.	581
Trichoptera (caddisflies)	
Hydropsyche sp.	1906
Polycentropus sp.	10
Diptera (true flies)	
Chironomidae (midges)	
Procladius sp.	50
Cricotopus sp.	250
Cardiocladius sp.	1233
Tipulidae (craneflies)	
Pedicia sp.	29
Empididae (dance flies)	19
Simuliidae (blackflies)	19
Lepidoptera (aquatic moths)	
Parargyractis sp.	10
Gastropoda (snails)	
Physa sp.	10
Oligochaeta (worms)	29
Hydracarina (aquatic mites)	29

Total Species	14
Total Organisms	4204
Diversity Index ($\bar{d}$)	2.080

Table D-3 (Continued). Upriver Drive Station Collected August 1, 1973.

Organism	Number of Organisms No./m^2
Plecoptera (stoneflies)	
Isogenus sp.	19
Ephemeroptera (mayflies)	
Baetis sp.	29
Trichoptera (caddisflies)	
Hydropsyche sp.	387
Polycentropus sp.	19
Diptera (true flies)	
Chironomidae (midges)	
Procladius sp.	89
Cardiocladius sp.	475
Cricotopus sp.	65
Tipulidae (craneflies)	
Pedicia sp.	29
Empididae (2 genera) (dance flies)	29
Lepidoptera (aquatic moths)	
Parargyractis sp.	19
Gastropoda (snails)	
Physa sp.	29
Hydracarina (aquatic mites)	77

Total Species	13
Total Organisms	1266
Diversity Index ($\bar{d}$)	2.335