CHROMIUM AND NICKEL DISTRIBUTION IN A SIMULATED AQUATIC SYSTEM

By

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CHAPTER I

INTRODUCTION

Metal pollution in water bodies may be caused by municipal effluents, industrial effluents like those of electroplating industries and drainage of mines work (Ajmal and Khan, 1984). These discharges are a problem of serious concern because of the toxic properties of heavy metals to aquatic life and their adverse effects upon water quality. Studies dealing with aquatic pollution by heavy metals are very important because they yield knowledge as to the behavior of these metals in the aquatic ecosystem as well as the risk of contamination to the aquatic biota and humans through the food chain.

Chromium and nickel are heavy metals usually present in municipal and industrial effluents. (Pickering, 1974; Mearns et al., 1976; Friedrich and Filice, 1976; Namminga and Wilhm, 1977; Pfeiffer et al., 1980.) Chromium is an essential element to animals; plants and humans (Mearns et al., 1976), but at high concentrations is toxic to aquatic organisms and is accumulated and transferred through the food chains Environmental Protection Agency (EPA, 1979). Nickel is less toxic than chromium and it is not accumulated in significant amounts by aquatic organisms (EPA, 1979).

This study was conducted to investigate the behavior of chromium and nickel in a simulated aquatic ecosystem similar to Lake Carl Blackwell. The water and sediment used in the experiment came from the lake. The green sunfish (Lepomis cyanellus) was selected as an organism representative of the aquatic biota of this lake. The sorption and desorption of chromium and nickel as well as the distribution coefficients of both metals in the different compartments of the aquatic ecosystem (water, sediment and fish) were examined. In addition, the percentage of each metal and their partitioning coefficient in the particulate and dissolved phase were calculated.

CHAPTER II

LITERATURE REVIEW

Chromium in the Environment

Chromium is found in natural waters at very low concentrations. In freshwaters, chromium concentrations have been found in the range of 1-2 µg/L; concentrations in marine waters are lower and range from 0.05 to 0.5 µg/L. Higher concentrations, from 5 to 50 µg/L, have been reported in contaminated rivers (Moore and Ramamoorthy, 1984). In the high Sierra Mountains in California 170 lakes were sampled and only two contained >5 µg/L of chromium. The pH of those lakes ranged from 4.7 to 7.3 (Bradford et al., 1968). Namminga and Wilhm (1977), measured longitudinal variations in the concentrations of some heavy metals, including chromium in Skeleton Creek, Oklahoma, and they compared the concentrations in cool and warm seasons. Chromium concentrations in the water during the winter season ranged from 0.7 to 3.0 µg/L. During the summer, concentrations ranged from 0.4 to 1.0 µg/L. In sediment the concentrations ranged from 1.3 to 6.3 µg/g in the winter season, while during summer these values ranged from 2.4 to 14.7 µg/g.

High chromium concentrations have been found in polluted freshwater areas. Pfeiffer et al. (1980) reported chromium concentrations in water, bottom sediments, and suspended particles from a tributary of the Iraja River, Rio de Janeiro where an electroplating industry discharges its untreated effluents. The total chromium concentrations in water, bottom sediments and suspended particles ranged between 140 to 80 x 10^3 µg/L, 142 x 10^4 to 543 x 10^5 µg/g and 221 x 10^4 to 6107 x 10^4 µg/g, respectively.

Chromium concentrations in water, sediment and fish have been analyzed by several investigators. Friant (1979), reported chromium concentrations ranging from <0.01 to 0.78 µg/g in fish, from <0.02 µg/g to 0.08 µg/g in sediments and from 2 to 3 µg/L in the water column of samples collected in a northern New England river. Mathis and Cummings (1973), determined the concentrations of selected metals including chromium in sediment water, and biota in the Illinois River. Chromium concentrations ranged from 2 to 87 µg/g in sediment and 5 to 38 µg/L in water. The mean concentration of chromium in carnivorous fish was 0.12 µg/g, whereas the mean concentration was 0.22 µg/g in omnivorous fish. These concentrations showed that significantly higher concentrations of chromium were present in omnivorous fish than in carnivorous fish. These results suggest that the trophic level of the fish species is an important factor in the incorporation of trace metals into fish. Murphy et al. (1978) concluded from a study on the cadmium and zinc content of fish from an industrially contaminated lake that regardless of the route of uptake (food or gill epithelia), concentrations attained by fish are species related.

Chromium concentrations also have been reported in the different organs of fish. Brooks and Rumsey (1974), analyzed muscles, liver, kidneys, heart, gonads, spleen and gills of 8 marine species from New Zealand and found the average concentrations of all 8 species to be 0.02, 0.1, 0.2, 0.3, 0.2, 1.2 and 0.5 mg/kg wet weight in the respective organs.

Chromium is readily transferred through the food chain. Baptist and Lewis (1969) studied the transfer of radiolabeled Cr(III) in an estuarine food chain and observed that although chromium was transferred through each trophic level, the concentrations declined as trophic levels increased.

Nickel in the Environment

The nickel content of sea water ranges from about 0.1 to 0.5 µg/L. In fresh water streams and lakes it usually varies from 3-17 µg/L (Nriagu, 1980). For large rivers in North America, the nickel concentration ranges from 0-71 µg/L (Durum and Haffty, 1963). Bradford et al. (1968) measured the trace and major elements of 170 High Sierra lakes in California and found from 0.3 to 1.8 µg/L of nickel in 17 of the samples. The pH of the lakes ranged from 4.7 to 7.3, with a mean and median value of 6.0 Steele and Wagner (1975) studied trace metals at 12 selected sampling stations in northern Arkansas, along a 130 mile stretch of the Buffalo River. Sampled nickel concentrations in the water ranged from 2.5 to 20 µg/L. In selected Kansas streams, nickel concentrations ranged from below detection limit (10 µg/L) to 92 µg/L (Angino et al., 1974).

Naturally occurring nickel concentrations in sediment were found in the average range from 12 µg/g (Lake Michigan) to over 750 µg/g (Northwest Territories, Canada) (Nriagu, 1980). Nickel concentrations in the five Great Lakes ranged from 10 to 249 µg/g for Lake Superior, 1.00 to 198 µg/g for Lake Michigan, 2.80 to 147.80 µg/g for Lake Huron, 8.70 to 120.60 µg/g for Lake Eric and 4.10 to 121.30 µg/g for Lake Ontario (Nriagu, 1980). Moore and Ramamoorthy (1984) reported high nickel concentrations, in the average range from 8 to 2700 µg/g; in 28 Sudbury Lakes (Canada).

Nickel is not accumulated in significant amounts by aquatic organisms. Nriagu (1980), showed some preliminary estimates of the average range of nickel in fish from uncontaminated and contaminated areas. For uncontaminated areas the average nickel concentrations in fresh water fish were from <0.2 to 2.0 μg/g on a wet weight basis. Nickel concentrations in the kidney and skin of marine fish found near sources of pollution were 51.6 μg/g and 163.9 μg/g, respectively.

The mean nickel concentration in carnivorous fish and omnivorous fish from the Illinois River were 0.12 μg/g and 0.17 μg/g, respectively (Mathis and Cummings, 1973). High nickel concentrations exceeding 70 μg/g, have been reported in marine fish collected from the northeast coast of England (EPA, 1979).

Chromium Behavior in Water

Chromium exists primarily in two oxidation states, hexavalent chromium Cr(VI) and trivalent chromium Cr(III). These compounds are the biologically and environmentally significant forms of the element, although they are chemically different. Hexavalent chromium is quite soluble in water and is always found as a component of a complex anion. The anionic forms may be chromate ($CrO_4^=$), hydrochromate ($HCrO_4^-$) or dichromate ($Cr_2O_7^=$). The chromate ion ($CrO_4^=$) is the most common form of hexavalent chromium present in natural waters at pH's >6.5. Trivalent chromium is a positively charged ion that tends to form stable complexes with negatively charged organic or inorganic species. Its solubility varies with the hardness and alkalinity values of the water (Taylor et al., 1979; EPA, 1979).

Interconversions of Cr(III) and Cr(VI) are frequent in natural waters.

Schroeder and Lee (1975) studied the potential transformation of chromium in natural waters and found that Cr(VI) is reduced by Fe(+2), dissolved sulfides and certain organic compounds bearing sulfhydryl groups. However, Cr(III) is oxidized rapidly by a large excess of MnO_2 and slowly by oxygen under natural water conditions. Under aerobic conditions, Cr(VI) is stable as a soluble form in natural waters. Under anaerobic conditions Cr(VI) is reduced to Cr(III) and is accumulated in sediments (Taylor et al., 1979).

Chromium tends to occur in aquatic systems in the settleable particulate phase. Young et al. (1982) concluded that, in the Onondaga Lake, New York, chromium remained predominantly attached to particles. Gibbs (1973) observed that chromium in the Yukon and Amazon Rivers was transported primarily in crystalline sediments. In the Iraja' River, Rio de Janeiro, chromium Cr(III) attached to particles was the main source of chromium transport through the water column.

Nickel Behavior in Water

The predominant oxidation state of nickel in natural water is the divalent ion, Ni(+2), which forms stable complexes with inorganic and organic ligands. Nickel's solubility exhibits a dependence on pH. At pH 5 to 9, the free ion, Ni(+2), dominates. Above pH 9, precipitation of the compounds that nickel forms with hydroxide or carbonate occurs. This occurrence might result in the accumulation of nickel on the suspended solids in the water column and, eventually, in the sediments.

The fate of nickel in the aquatic ecosystem is influenced by its reactions with soluble species and with particles. Some possible mechanisms that influence these reactions are acid-base interaction, oxidation-reduction reactions, formation of metal-inorganic complexes and metal-organic complexes (Nriagu, 1980). In Onondaga Lake, 75% of the nickel load was in a dissolved form. After entering the lake the nickel remained mainly in the dissolved form (Young et al., 1982). Perhac (1972) found in two streams in Tennessee that 90% of nickel was in the dissolved form while less than 10% in the particulate form and less than 1% in the colloidal form.

Chromium and Nickel Behavior in Sediment

The adsorption of chromium by clay minerals is affected by pH. Griffin et al. (1977) found that adsorption of Cr(VI) decreased as the pH increased. However, the adsorption of Cr(III) increased as the pH increased. In addition, Cr(III) is adsorbed more strongly by clay than is Cr(VI).

Steele and Wagner (1975) found incorporation of chromium by sediment with quartz and chert grains which were coated with hydrous iron oxide. The correlation between chromium and iron is a result of the fact that $Fe(OH)_3$ is precipitated along with $Cr(OH)_3$. Coprecipitation of these materials may increase the speed with which chromium is removed from solution (EPA, 1979).

Nriagu (1972), mentioned several factors that may control the fixation of nickel and other heavy metals in soil and water. The factors are: nickel association with organic matter, clay or carbonate, sorption or desorption of nickel from hydrous Mn or Fe oxides and, finally, precipitation of nickel as nickel oxide or nickel hydroxide. Angino et al. (1974) and Steele and Wagner (1975) stated that significant correlations between nickel and both manganese and iron on the suspended sediment suggested coprecipitation of nickel with iron and manganese oxides.

Jackson and Skippen (1978) performed a laboratory model experiment to describe the behavior of some metals, including nickel, at a simulated sediment-water boundary. In a desorption experiment, they observed that fulvic and humic acids are able to remove nickel from the sediment phase, including both metal hydroxides and metal adsorbed to clay, although the reaction appears to be kinetically hindered, specially at basic pH values. In the sorption experiment they found that nickel was stabilized in solution by humic and fulvic acids in the presence of clay.

Chromium and Nickel Toxicity in Fish

Most of the fresh water toxicity data, both lethal and sublethal, indicate hexavalent chromium to be more toxic than trivalent chromium.

Benolt (1976), studied the toxic effects of hexavalent chromium on brook trout (*Salvelines fontinalis*) and rainbow trout (*Salmo gairdneri*). A chromium concentration of 0.35 mg/L increased the mortality in brook trout alevins, whereas retarded growth of young brook trout occurred at the lowest concentration tested (0.01 mg/L). In rainbow trout the same effects were observed at the respective chromium concentrations of 0.34 mg/L and 0.10 mg/L. A hexavalent chromium concentration of 3.95 mg/L affected the survival of fathead minnows (*Pimephales promelas*), with all chromium concentrations tested (which were as low as 0.018 mg/L) causing retarded early growth of first generation fish. However, this effect was only temporary (Pickering, 1980).

The pH of the media influences the site of chromium toxicity in fish. Morphological changes were observed in rainbow trout (*Salmo gairdneri*) with exposure to chromium(VI)at different concentrations for

96 h and at decreasing pH's in the range of 7.8 to 6.5. At pH 7.8 histological damage was observed to the gills, kidney and stomach, whereas at pH 6.5 histological damage appeared to be restricted to the gills only (Van Der Putte et al., 1981).

Temperature changes can increase the toxicity of chromium. Smith and Heath (1979) found that changes in temperature from 5°C to 30°C caused a decrease in the 24 h LC50 from 300 to 110 mg/L for gold fish (Carassius auratus). However, the effect in rainbow trout was just the opposite, as the LC50 value increased from 20 to 90 mg/L as the temperature increased.

Water hardness also influences chromium toxicity. The TLM 96 h of hexavalent chromium in soft water (20 mg/L as $CaCO_3$) was 17.6 mg/L for fathead minnows (Pimephales pomelas) and 118 mg/L for blue gills (Lepomis machrochirus). The TLM 96 hr in hard water (360 mg/L as $CaCO_3$) was 27.3 mg/L for fathead minnows and 133 mg/L for bluegills (Pickering and Henderson, 1966).

Muramoto (1981) demonstrated that the addition of complexans, trisodium salt of nitrilotriacetic acid (NTA) or tetrasodium salt of ethylenediamine tetraacetic acid (EDTA), decreased the toxicity of chromium to carp (Cyprinus carpio). Inhibition of metal accumulation in the gills was also observed with the addition of the complexes.

Tolerance of fish toward several salts of nickel varies with the species, pH, water hardness, synergism of other metals, and other factors (McKee and Wolf, 1963; Pickering and Henderson, 1966).

Rehwoldt et al. (1971) studied acute toxicity of copper, nickel and zinc ions to some Hudson River fish species. The River water had a hardness of 53 mg/L as $CaCO_3$ and a pH of 7.8. The TLM 96 hr of nickel was found to be 46.2 mg/L for the banded killfish (Fundulus diaphanus), 6.2 mg/L for the striped bass (Rocus saxatilis), 8.1 mg/L for the pumpkin seed (Lepomis gibbosus), 13.6 mg/L for the white perch (Roccus americanus), 13 mg/L for the American eel (Anguila rostrata), and 10.6 mg/L for the carp (Cyprinus carpio).

Pickering and Henderson (1966) determined the acute toxicity of the salts of several metals, including nickel, on four species of warm water fish. The tests conducted in soft water (20 mg/L as $CaCO_3$) using nickel chloride as test compound and fathead minnows and bluegills as the fish species, had a TLM 96 hr which varied from 5.18 mg/L for fathead minnows (Pimephales promelas) to 5.36 mg/L for bluegills (Lepomis macrochirus). When tests were conducted in hard water (360 mg/L as $CaCO_3$). The TLM 96 hr value of nickel varied from 39.6 mg/L for bluegills to 44.5 mg/L for fathead minnows.

Rainbow trout (Salmo gairdneri) have been used to study the sublethal effects of nickel exposure. Nickel concentrations of 2 mg/L to 3.2 mg/L were maintained for 3.5 days and caused a reduction in the diffusion capacity of the gills and an increase in the thickness of the lamellar membrane (Hughes and Perry, 1979). Becker and Walford (1980) demonstrated that the thermal resistance of rainbow trout to elevated temperatures was significantly suppressed when exposed to nickel at a concentration of 1.5 mg/L, a sublethal dosage for 7 to 21 days.

Nickel toxicity may be reduced by addition of complexans. Muramoto (1983), studied the effect of complexans (NTA, EDTA) on the toxocity of nickel chloride. At a concentration of 30 mg/L as nickel, the mortality was 60% within 24 hr and 80% within 48 hr. In the case of nickel sulfate, at a concentration of 30 mg/L as Ni, the mortality was 30% within

24 hr and 50% within 48 hr. In contrast, for the nickel chloride plus-complexan groups, the mortality was 20% at the concentration of 30 mg/L as Ni + EDTA within 24 hr, 30% within 48 hrs and 20% within 48 hr using 30 mg/L as Ni + NTA. In the case of nickel sulfate plus-complexan groups, the mortality was observed to be 10% within 48 hours at 20 mg/L as nickel + EDTA, 20% at 30 mg/L as Ni + EDTA within 48 hours and 20% at 30 mg/L as Ni + NTA within 48 hours.

CHAPTER III

MATERIALS AND METHODS

This study was conducted in parallel simulated aquatic systems. The ecosystems were set up in two 88 liter rectangular aquaria. One aquarium served as the experimental unit, that was feed metals, while the other aquarium functioned as a control. The identical systems imitated the environmental conditions of Lake Carl Blackwell, located 11 km west of Stillwater, Oklahoma. This lake is used for recreational purposes and also serves as a water supply for Stillwater.

Fish used in this experiment were Green Sunfish (<u>Lepomis</u> <u>cyanellus</u>) collected from farm ponds located just below the outflow from Lake Carl Blackwell. The fish were provided by Dr. Glen Gebhart of Langston University. Sediment was collected off the end of a pier located in a recreational area on the south shore of the lake. The sediment was collected with an Ekman Dredge and was used to cover the bottom of the aquaria. Each system received about 12,000 g of sediment (dry weight) achieving a depth of about 7.6 cm. The water for the experiment was taken from the old cascada aerator, that today is used as a prechlorination basin, located at the Oklahoma State University water treatment plant. The water used in this investigation was taken prior to chlorine addition. The water plant is situated 3 km west of the Environmental Engineering Laboratories where the aquaria were set up. Water from the treatment plant was pumped into a 190L plastic tank and trucked back to the laboratory. The water was then repumped into a 568 L cylindrical plastic tank located inside the laboratory by means of a Mini-vac pump, model M40K. Delivery into the aquaria was accomplished using a Mil-Royal controlled volume pump at 10 ml/min (14.4 L/day). The hydraulic retention time of each system was 6.1 days. Oxygen was delivered to the aquaria by airstones, using laboratory compressed air.

The nickel and chromium solutions were prepared from reagent grade Nickelous Sulfate and Potassium Dichromate, respectively. Predetermined quantities of the reagent chemicals were dissolved in distilled water to prepare a metal solution containing 0.5 mg/L of each metal.

Delivery of the metallic solution into the experimental aquarium was accomplished by means of a Cole Palmer 7013 variable speed flex pump, at the rate of 6 ml/min. The pump was placed on a timer and pumped for 15 seconds every 2 minutes. The metal solution was pumped into a tee located in the raw water feed line and the turbulence in the line was used to create a homogenous solution prior to being discharged into the experimental unit (Figure 1).

The systems were illuminated by two 40W Agro-lite fluorescent bulbs that were suspended above each aquaria. The photoperiod was controlled by a timer to give 15 hours of light and 9 hours of darkness. Twenty-five fish were placed in both the experimental and control tanks at the beginning of the study. The fish were acclimated to the aquaria for a period of 30 days prior to the beginning of the experiment. Originally aquatic plants were also placed in both aquaria but those died during the acclimation period.

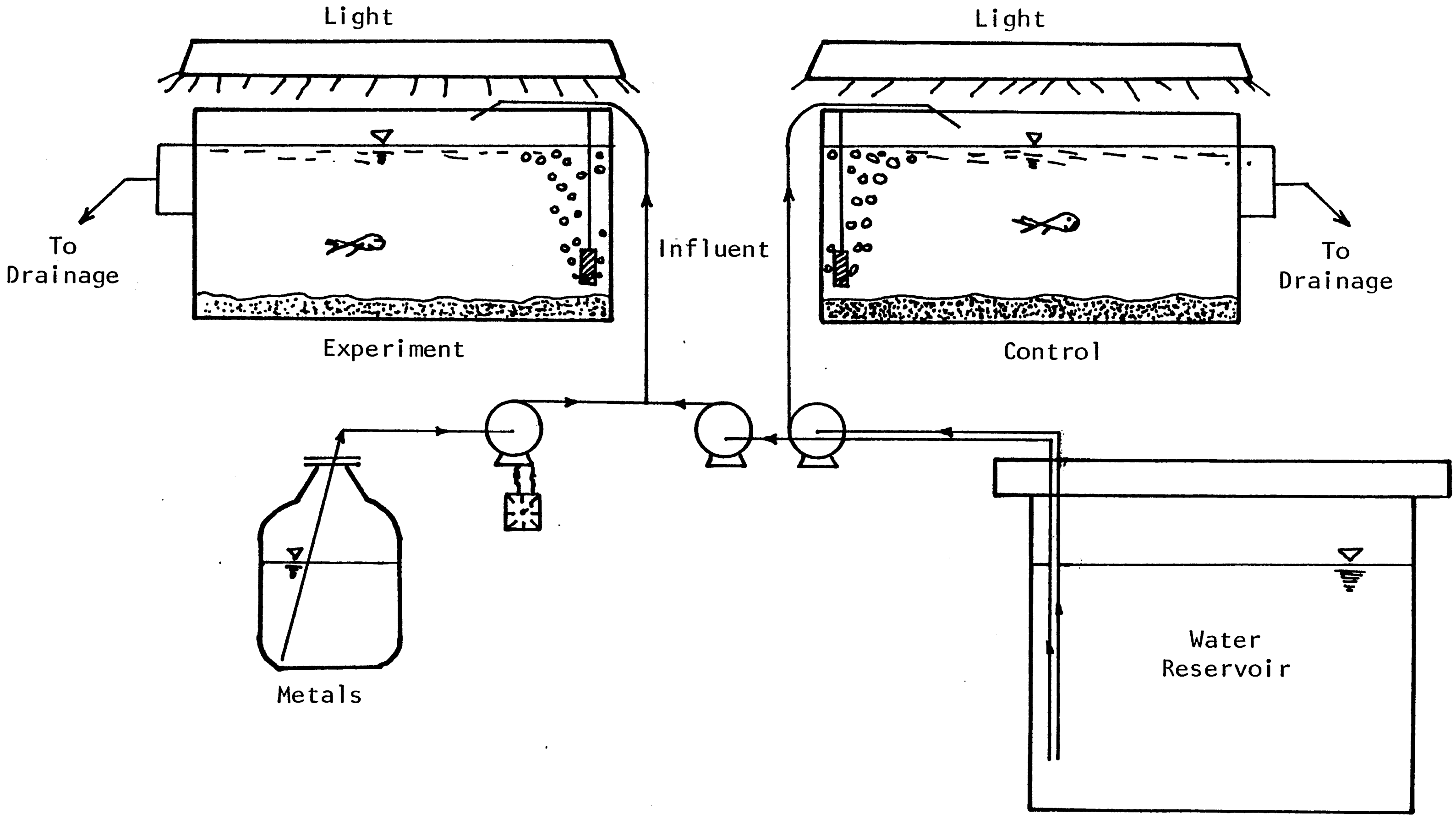

Figure 1. Schematic Diagram of Experimental System

Procedure

The experiment was divided into two phases: 1) a sorption phase (both metals added) and 2) a desorption phase (no metals added). The sorption phase was performed for a period of 73 days (12 hydraulic retention times) and the desorption phase for a period of 52 days (8.5 hydraulic retention times). A total of 23 samples of each component in the systems (sediment, water and fish) were taken from each aquaria during the experiment. Table I shows the sampling schedule for water, fish and sediment used in this experiment.

All samples were prepared for metal analysis by a wet digestion procedure. All chemicals used in the various digestion procedures were of reagent quality or better. Water samples were digested with concentrated nitric acid using the technique recommended by EPA (1983).

Sediment samples were digested on a hot plate at approximately 100°C with nitric acid and hydrogen peroxide, following the procedure described by Krishnamurty et al. (1976). After digestion, water samples and sediment samples were diluted to a 50 ml volume with distilled deionized water. Following Atomic Absorption analysis the metal concentraitons in the sediment and the water samples were calculated using the following relationship:

$$\frac{\text{mg/L in Solution} \times 0.05 \text{ L}}{\text{Sample Weight (q) or Sample Volume (L)}}$$

The weight, length and height of each fish were measured prior to analysis. This data is set out in Appendix A.

The whole fish was homogenized with the addition of a volume of water approximately equal to their weight in grams. Therefore, the metal concentrations represent a total body burden. Samples were dried over night at

TABLE I

SAMPLING SCHEDULE FOR WATER, FISH AND SEDIMENT

Sample No.	Sample Taking	Day Intervals	Sampling Date
1	3	5	8/11/84
2	2	9	8/15/84
3	1	13	8/19/84
4	2	17	8/23/84
5	1	29	9/04/84
6	1	43	9/18/84
7	1	55	9/30/84
8	1	73	10/18/84
9	1	79	10/24/84
10	1	83	10/28/84
11	1	89	11/03/84
12	1	93	11/07/84
13	1	97	11/11/84
14	1	101	11/15/84
15	3	111	11/25/84
16	2	125	12/09/84

$105^{\circ}C$ and then the dry weight was determined.

Fish samples were digested on a hot plate at low digestion temperatures ($<100^{\circ}C$) with nitric acid and perchloric acid (5:1), using the technique recommended by Leonard (1971). After digestion, the residues were dissolved in 10 ml of deionized water.

Upon completion of the analysis, the metal concentrations were determined with the following relationship:

$$\frac{\text{mg/L in Solution} \times 0.01 \text{ L}}{\text{Sample Dry Weight (g)}} = \text{mg/g of Metal in Sample}$$

The concentration of metal in the sample material was expressed on a wet weight basis. The following method was used to convert the data from a dry weight to a wet weight basis. The weight of the individual fish plus the added water was determined for the homogenized sample. From this the percentage of the total weight due to the added water was calculated. A portion of this fish and water mixture was then placed in a 100 ml beaker and weighed. Since this mixture had been blended to a homogeneous state, the percentage of water in the subsample placed in the 100 ml beaker was assumed to be the same as the original homogenized mixture. The weight of the subsample was then multiplied by the percentage of added water to determine the weight of added water in grams. This value was then subtracted from the total weight of the subsample to determine the wet weight of the fish, in grams, in the subsample. As stated previously the subsample was then dried at $105^{\circ}C$ overnight and reweighed to determine the dry weight. A small amount of this dry weight, 0.25 grams, was then acid digested for metal analysis. To convert the metal concentration from a dry weight to a wet weight basis, the 0.25 g sample used in the ecuation to calculate the metal concentration, was multiplied by the ratio of the calculated wet weight of the subsample to the oven dried weight of the fish in the subsample. This new value was then used in the equation to obtain the concentration of metals in the fish on a wet weight basis. An example calculation is shown in Appendix B.

Reagent blanks were analyzed following the same procedure used for the samples, standard solutions of chromium and nickel were prepared by dilutions of 1,000 mg/L stock solutions (Fisher Scientific Company).

Metal analysis of the samples was performed by Atomic Absorption Spectrophotometry (Perkin Elmer Model 500), using both flame and flameless techniques. The Atomic Absorption unit was equipped with a Graphite Furnace (HGA 500). Some samples were analyzed using the flame when the Graphite Furnace was malfunctioning. A metal mass balance of the system was calculated using the following relationship:

Accumulation Within System Soil = Input of Metal-Metal Concentration in Fish-
Metal Concentration in Effluent Water

As part of the data analysis the distribution coefficients (kd) were calculated. This coefficient may be defined as the ratio of the mass of contaminant in two phases. Those phases are fish, sediment and water. Four combinations of these phases were calculated:

Unfilter Water/Filter Water

Sediment/Water

Fish/Water

Fish/Sediment

As background information, the natural concentration of chromium and nickel in water, sediment and fish were determined before starting the experiment.

The sediment was analyzed to determine the percentage of sand, clay and silt present, by the sieve and hydrometer analysis. The sieve analysis was performed using the U.S. Standard Sieve Series seives. The hydrometer analysis was accomplished using a Fisher Scientific hydrometer.

Temperature, pH and dissolved oxygen were recorded frequently during the sorption and desorption phases of the experiment. The pH was determined using an Orion pH electrode and a Beckman Model 501 pH meter. The dissolved oxygen was measured using an Orion Model 97-8700 02 electrode. Raw water quality data, including, pH, hardness, temperature, alkalinity and turbidity, were obtained from the Oklahoma State University Treatment Plant on the dates when freshwater was obtained and transported back to the Environmental Engineering Laboratories. The Total Organic Carbon content of the raw water was determined by using the O.I. Model 524D Total Organic Carbon Analyzer.

CHAPTER IV

RESULTS

Table II shows the chromium and nickel concentrations in water, sediment, and fish samples before the start of the experiment. The sediment sample had the highest concentration of both metals, 20.5 µg/g of chromium and 15 µg/g of nickel. The metal concentrations in fish samples were 0.7 µg/g of chromium and 0.40 µg/g of nickel. The chromium and nickel concentrations in water samples were <100 µg/L of chromium and <150 µg/L of nickel, these concentrations equal the detection limit of flame atomic absorption.

The results of the water quality analyses, from both tanks, during the experiment are shown in Table III. The suspended solid concentration was 140 mg/L in both tanks at the end of the experiment. Values of pH, temperature and dissolve oxygen also were similar in both tanks. The values shown in the table are the average of data collected throughout the experiment. The water quality analyses, of the raw water, that were collected over the whole experiment are presented in Table IV.

Composition of the sediment was determined to be 45% silt, 55% sand and 15% clay. The Biochemical Oxygen Demand (BOD) of sediment was 120 mg/g. and its final pH was 7.79.

Table V shows the total chromium concentrations in the water, sediment and fish samples during the sorption phase. The chromium concentration in the water was <100 µg/L on day 0; from day 5 to day 43 this

TABLE II

CHROMIUM AND NICKEL CONCENTRATIONS IN WATER, SEDIMENT AND FISH SAMPLES BEFORE THE START OF THE EXPERIMENT

	Chromium Concentration	Nickel Concentration
Water	<100 μg/L	<150 μg/L
Sediment	20.5 μg/g	15 μg/g
Fish	0.7 μg/g (Wet Weight)	0.40 μg/g(Wet Weight)

TABLE III

WATER QUALITY ANALYSES DURING THE EXPERIMENT

Parameters	Control Tank	Experiment Tank
Suspended solids, mg/L	140	140
pH	7.44-8.04	7.54-8.06
Temperature °C	19.88*	19.80*
Dissolved Oxygen, mg/L	7.80*	7.88*
TOC, mg/L	9.83*	10.58*

*Average values.

TABLE IV

WATER QUALITY ANALYSIS OF THE RAW WATER

Parameter	Sorption $\bar{X}$ ± Std. Dev.	Desorption Phase $\bar{X}$ ± Std. Dev.
Alkalinity, mg/L as $CaCO_3$	132.3 ± 4.2	135.4 ± 2.0
Hardness, mg/L as $CaCO_3$	158.6 ± 4.3	160.3 ± 0.5
Turbidity, NTU	16.6 ± 1.9	19.8 ± 1.9
pH	7.7 - 8.7	7.6 - 8.7
Temperature, °C	27.7 ± 0.4	17.2 ± 1.4

TABLE V

CHROMIUM CONCENTRATION DURING SORPTION PHASE

Sample No.	Day	Water (μg/L)	Sediment (μg/g)	Fish (μg/g)
0	0	<100	20.5	0.70
1	5	100	22.0	1.20
2	9	100	22.5	1.00
3	13	100	26.4	1.25
4	17	100	25.3	0.60
5	29	100	37.0	1.00
6	43	100	73.0	1.00
7	55	110	90.0	1.20
8	73	120	150.0	1.40

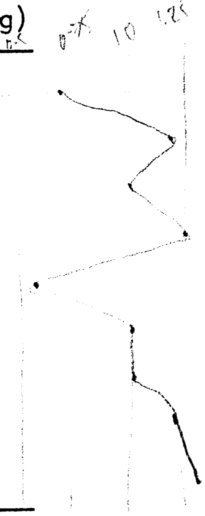

TABLE VI

CHROMIUM CONCENTRATION DURING DESORPTION PHASE

Sample No.	Day	Water (μg/L)	Sediment (μg/g)	Fish (μg/g)
9	79	200	63.0	0.80
10	83	180	44.0	0.60
11	89	180	43.0	0.50
12	93	160	119.0	0.60
13	97	200	49.0	0.50
14	101	300	50.0	0.50
15	111	300	43.0	1.00
16	125	300	40.0	0.30

concentration was 100 µg/L, the highest concentration reached on this phase was 120 µg/L, on day 73 (Figure 2). In the sediment the chromium concentration increased 20.5 µg/g on day 0 to a peak concentration of 150 µg/g on day 73 (Figure 3). Uptake of chromium by the fish was fast. On day 0 the concentration was 0.7 µg/g, by day 5 the concentration increased up to 1.20 µg/g, but by day 17 the concentration decreased to 0.60 µg/g. An apparent steady concentration was observed between days 29 and 43. By day 55 the concentration was 1.20 µg/g. At the end of sorption phase, on day 73, the maximum concentration observed was 1.40 µg/g (Figure 4).

Chromium concentrations during the desorption phase are shown in Table VI. At the beginning of the desorption phase, day 79, the chromium concentration in the water was 200 µg/L. An apparent equilibrium concentration of 300 µg/L was reached between days 101 and 125 (Figure 2). Release of chromium from the sediment decreased the concentration from 63 µg/g on day 79 to 40 µg/g by day 125 (Figure 3). A very high concentration (119 µg/L) was observed on day 93, the control sample taken on the same day also contained a high concentration of chromium (Figures 3, and 5). Levels of chromium accumulated by fish declined from 0.8 µg/g on day 79 to 0.50 by day 97. Between days 101 and 111 an equilibrium concentration of 1.0 µg/g was observed, but the concentration decreased to 0.30 µg/g by day 125 (Figure 4).

Table VII and Figure 6 shows the nickel concentrations during the sorption and desorption phases. Water nickel concentrations increased from <150 µg/L on day 0 to 210 µg/L by day 43. But on day 55 the concentration decreased to 200 µg/L and by day 73 (last day of sorption) the concentration was 180 µg/L. The accumulation of nickel in the sediment

TABLE VII

NICKEL CONCENTRATION DURING SORPTION PHASE

Sample No.	Day	Water (μg/L)	Sediment (μg/g)	Fish (μg/g)
0	0	<150	15.0	0.4
1	5	160	41.3	1.4
2	9	165	15.0	1.0
3	13	150	26.5	1.4
4	17	170	19.3	0.8
5	29	190	95.0	1.5
6	43	210	60.0	1.1
7	55	200	110.0	1.5
8	73	180	140.0	1.5

TABLE VIII

NICKEL CONCENTRATION DURING DESORPTION PHASE

Sample No.	Day	Water (μg/L)	Sediment (μg/g)	Fish (μg/g)
9	79	250	90.0	1.1
10	83	200	70.0	0.6
11	89	240	80.0	0.7
12	93	250	120.0	0.9
13	97	200	80.0	0.8
14	101	210	80.0	0.5
15	111	237	73.0	0.5
16	125	235	70.0	0.4

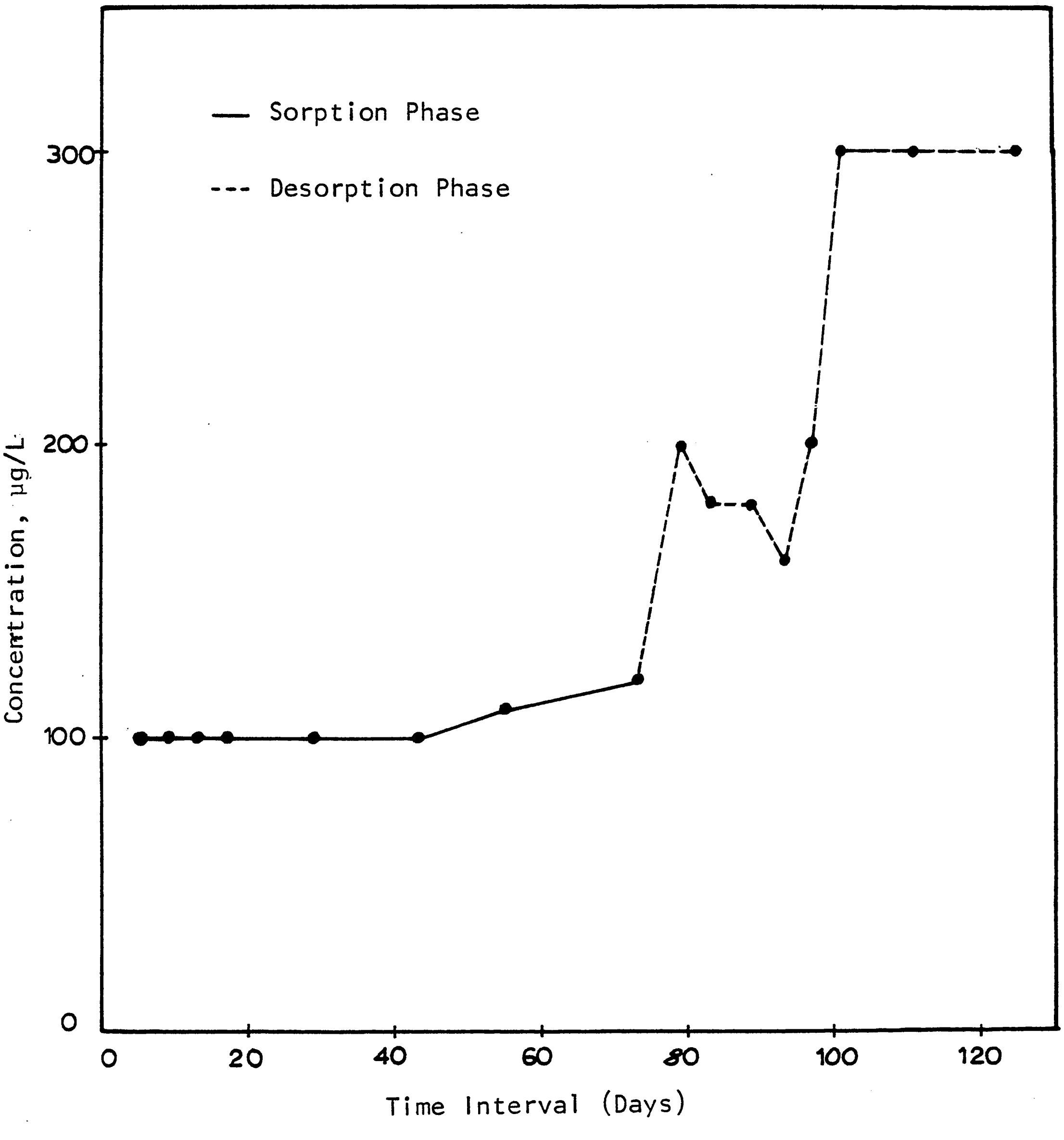

Figure 2. Chromium Concentrations in Water During Sorption and Desorption Phases

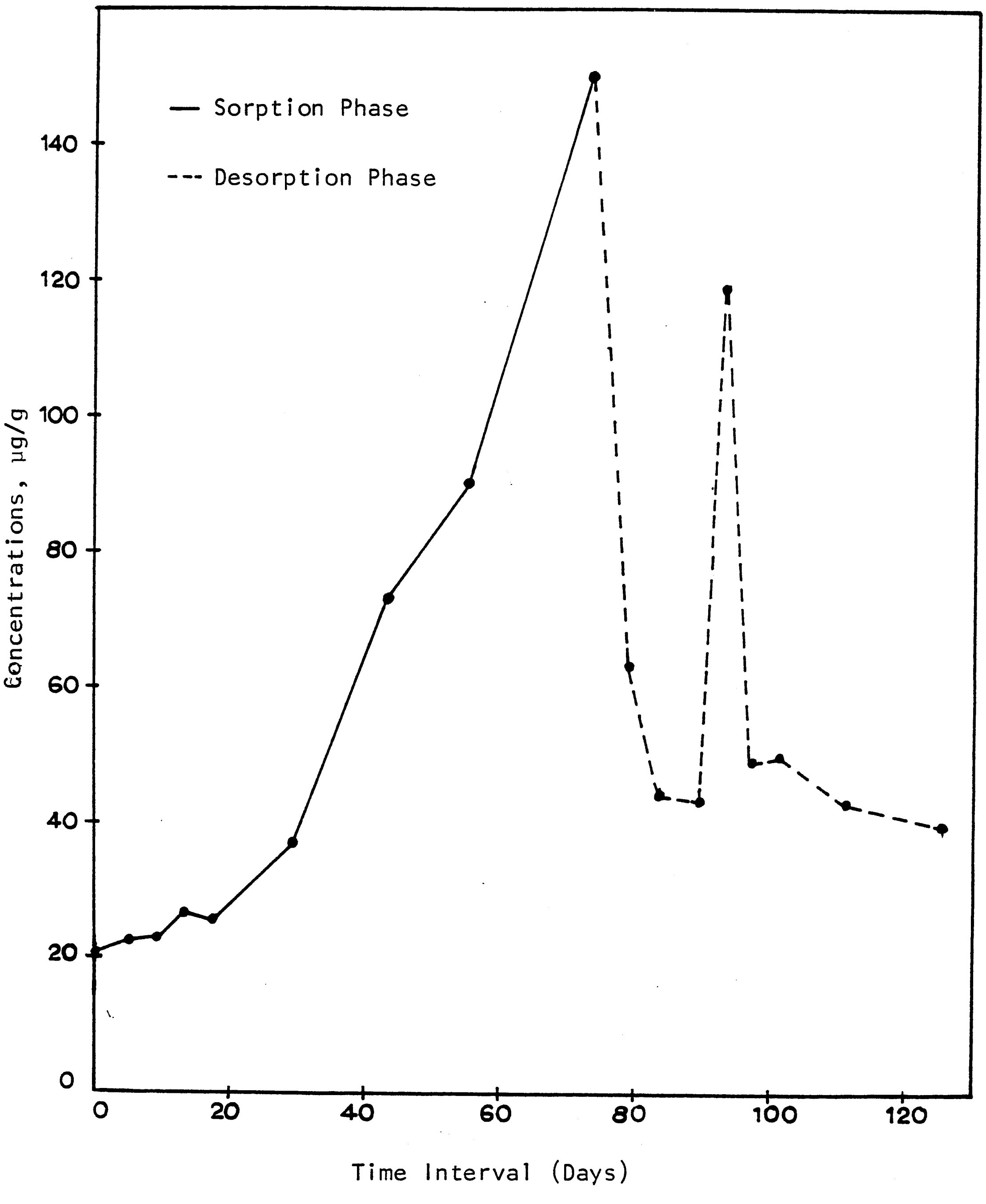

Figure 3. Chromium Concentrations in Sediment During Sorption and Desorption Phases

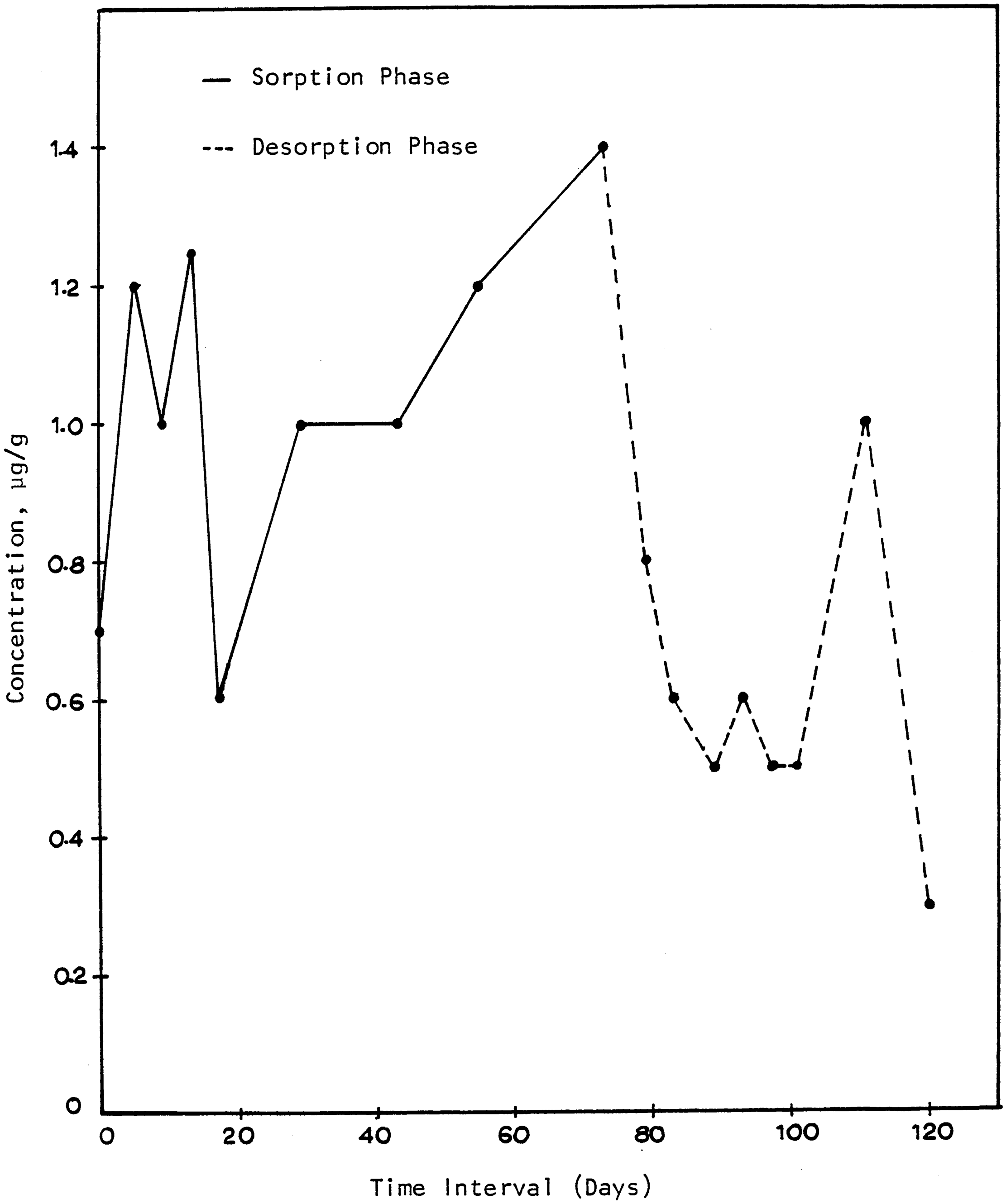

Figure 4. Chromium Concentrations in Fish During Sorption and Desorption Phases

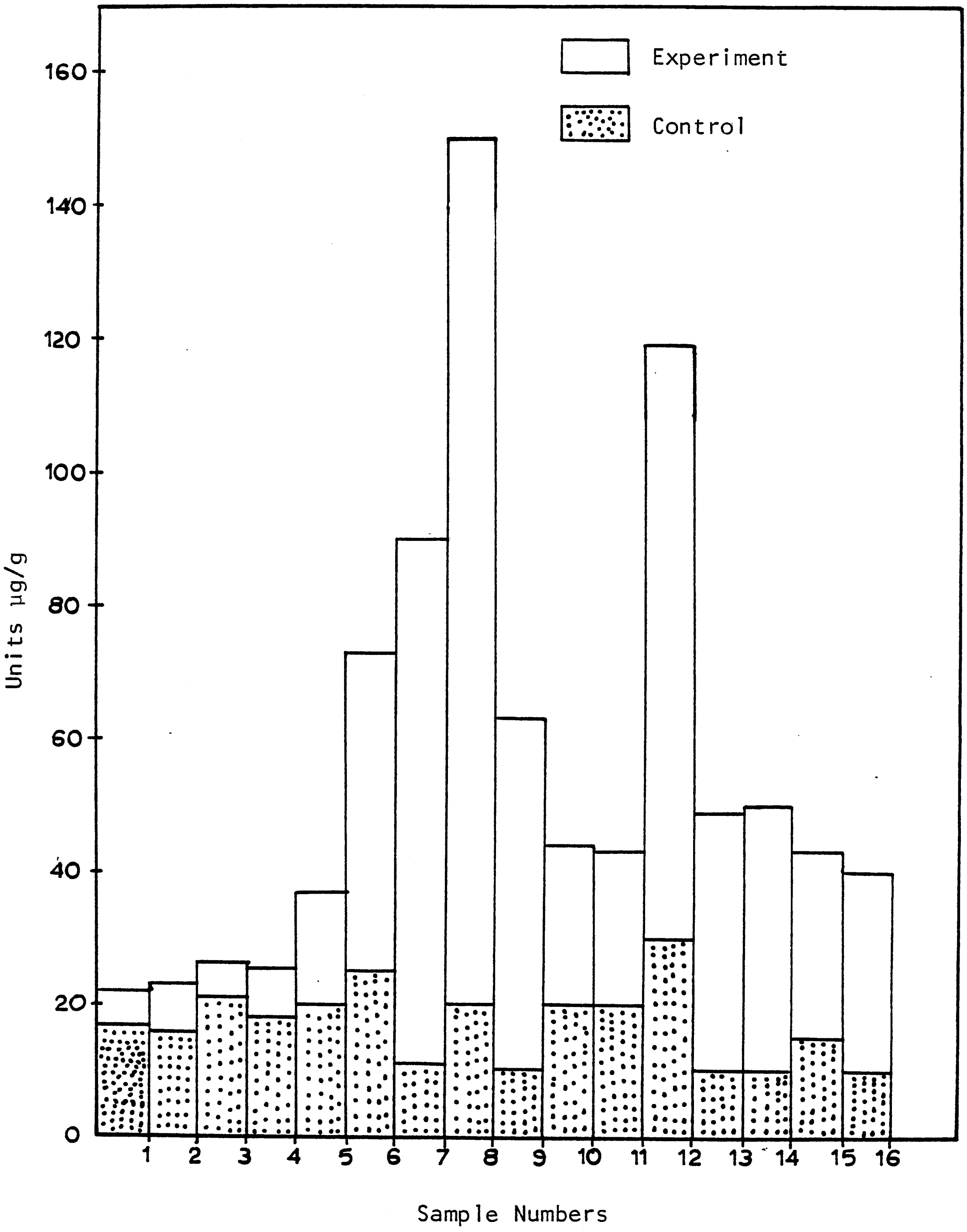

Figure 5. Chromium Concentration in Sediment From Experimental and Control Units

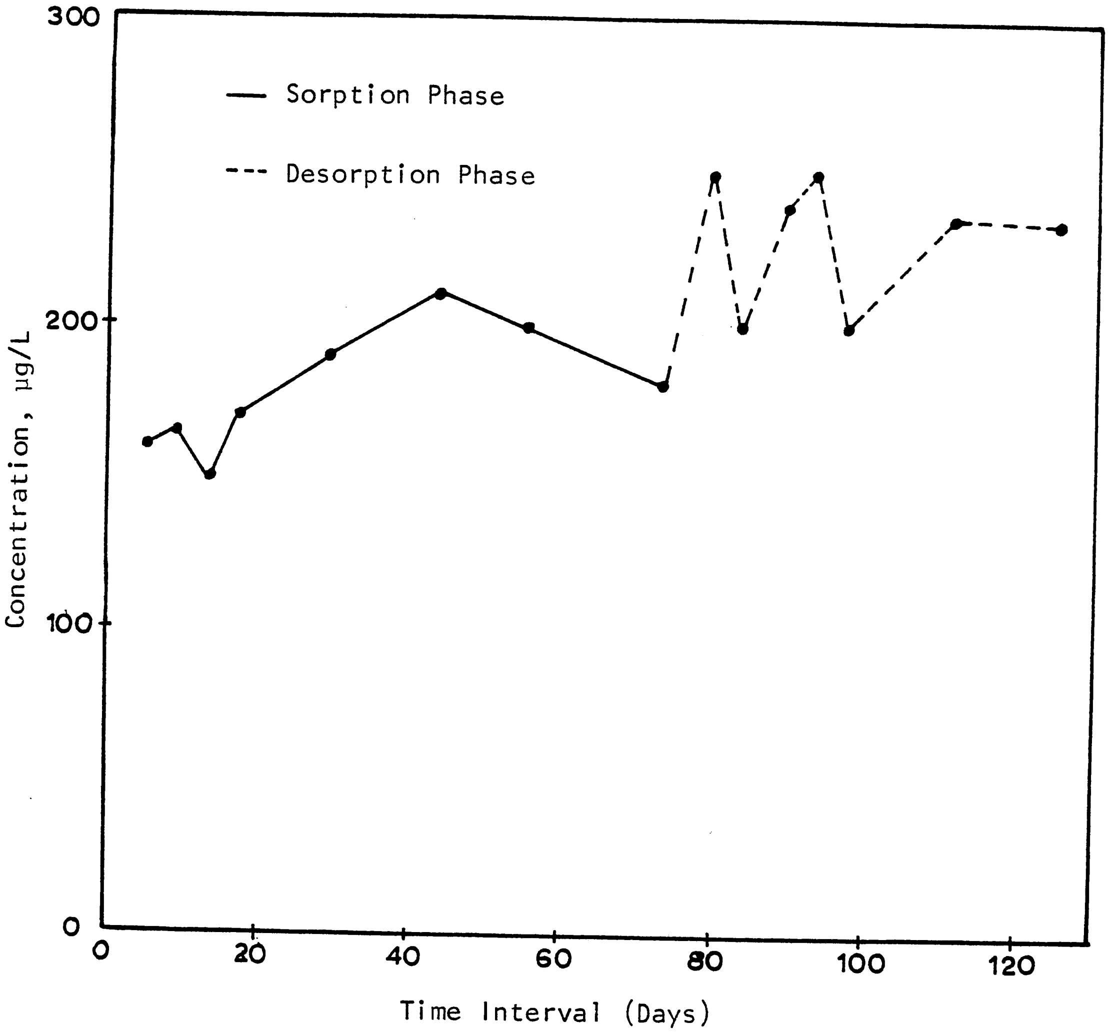

Figure 6. Nickel Concentration in Water During Sorption and Desorption Phases

increased from 15 μg/g on day 0 to 140 μg/g by day 73 (Table VII, Figure 8). The nickel concentration in the fish was 0.4 μg/g on day 0. On day 5 the concentration increased to 1.4 μg/g. Eventually an equilibrium concentration of 1.5 μg/g was observed from day 55 to 73 (Figure 8).

During the desorption phase (Table VIII) the nickel concentration in the water decreased from 250 to 235 μg/L (Figure 6). In the sediment the concentration decreased from 90 μg/g on day 79 to 70 μg/g by day 125. On day 93 a concentration of 120 μg/g was observed (Figure 7). In the control sample a high concentration was also determined (Figure 9). The nickel concentration in the fish at the first data point of the desorption phase (79th day) was 1.1 μg/g. A constant concentration was reached between days 101 and 111, and by day 125 a decrease in concentration to 0.40 μg/g occurred (Table VIII and Figure 8).

A chromium and nickel mass balance was calculated using the following relationship:

$$\text{Accumulation within system (soil)} = \text{Input of Metal} - \text{Accumulation in Fish} - \text{Metal Concentration in Water}$$

For chromium the mass balance calculation was:

$$390.8 \text{ mg} = 556.6 \text{ mg} - .622 \text{ mg} - 167.5 \text{ mg}$$

$$390.8 \text{ mg} = 388.4 \text{ mg}$$

Recovery of chromium was 101%. For nickel the mass balance calculation was:

$$493 \text{ mg} = 569.2 \text{ mg} - .698 \text{ mg} - 207.9 \text{ mg}$$

$$493 \text{ mg} = 360.6 \text{ mg}$$

Recovery of nickel was 136%.

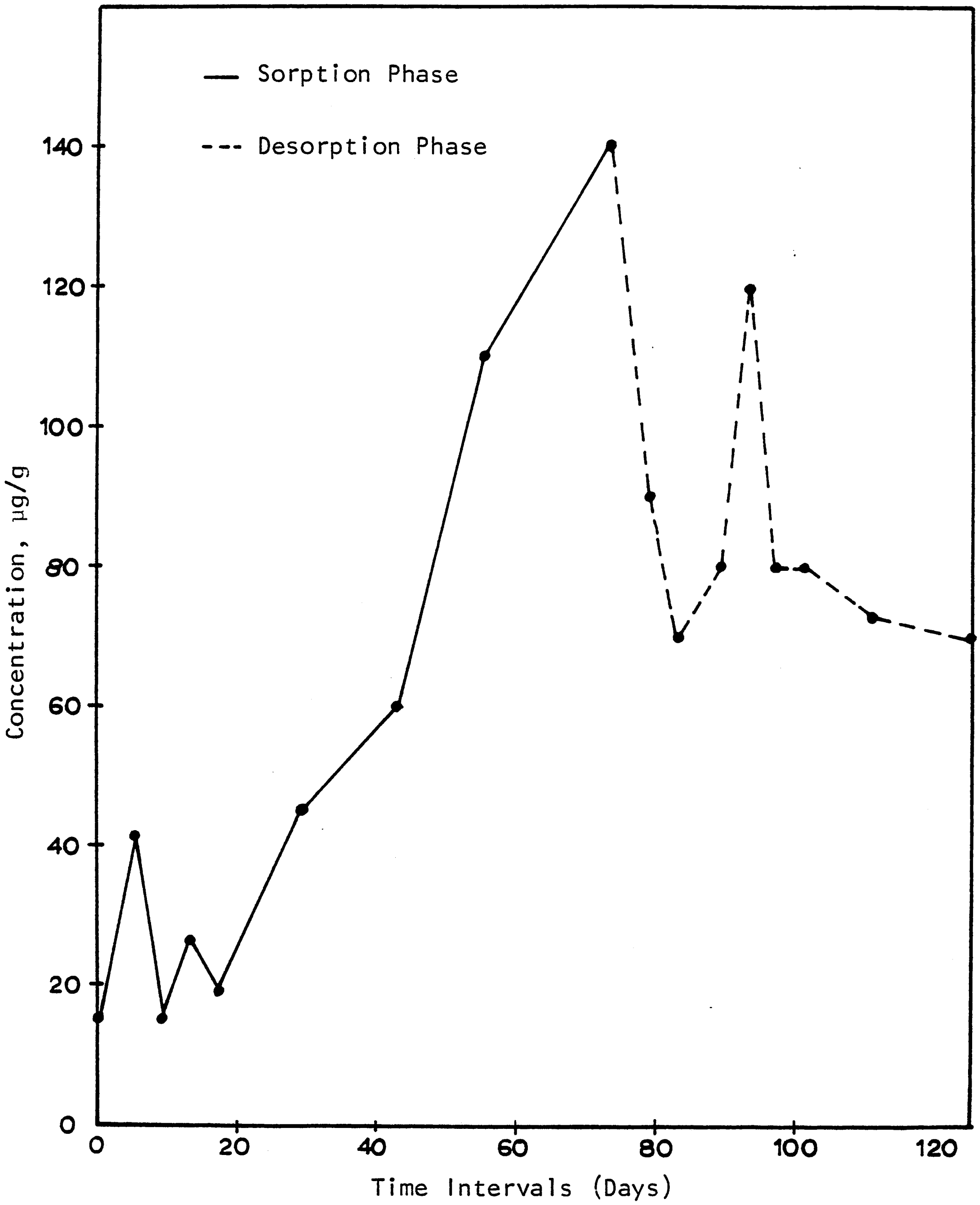

Figure 7. Nickel Concentrations in Sediment During Sorption and Desorption Phases

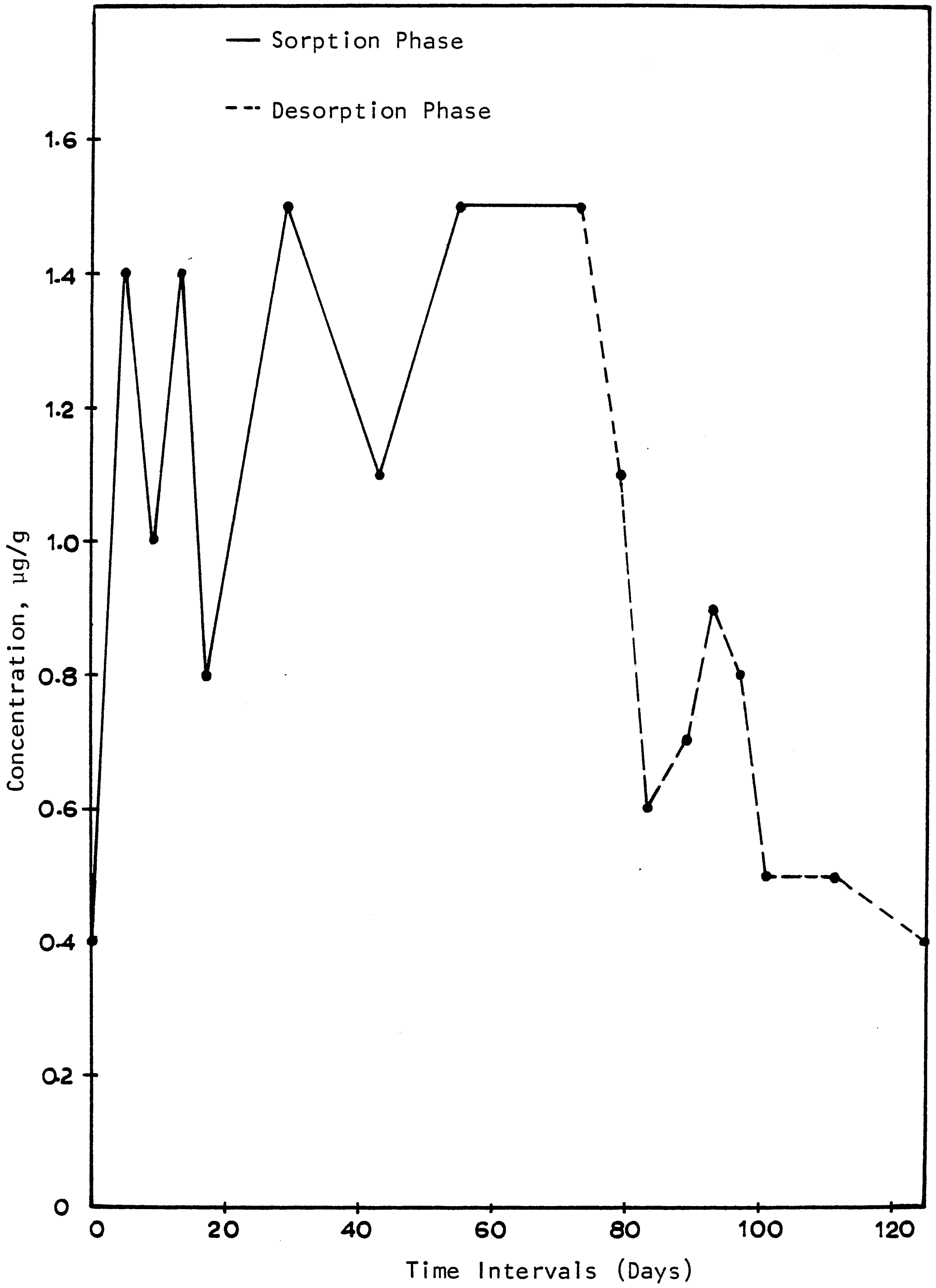

Figure 8. Nickel Concentrations in Fish During Sorption and Desorption Phases

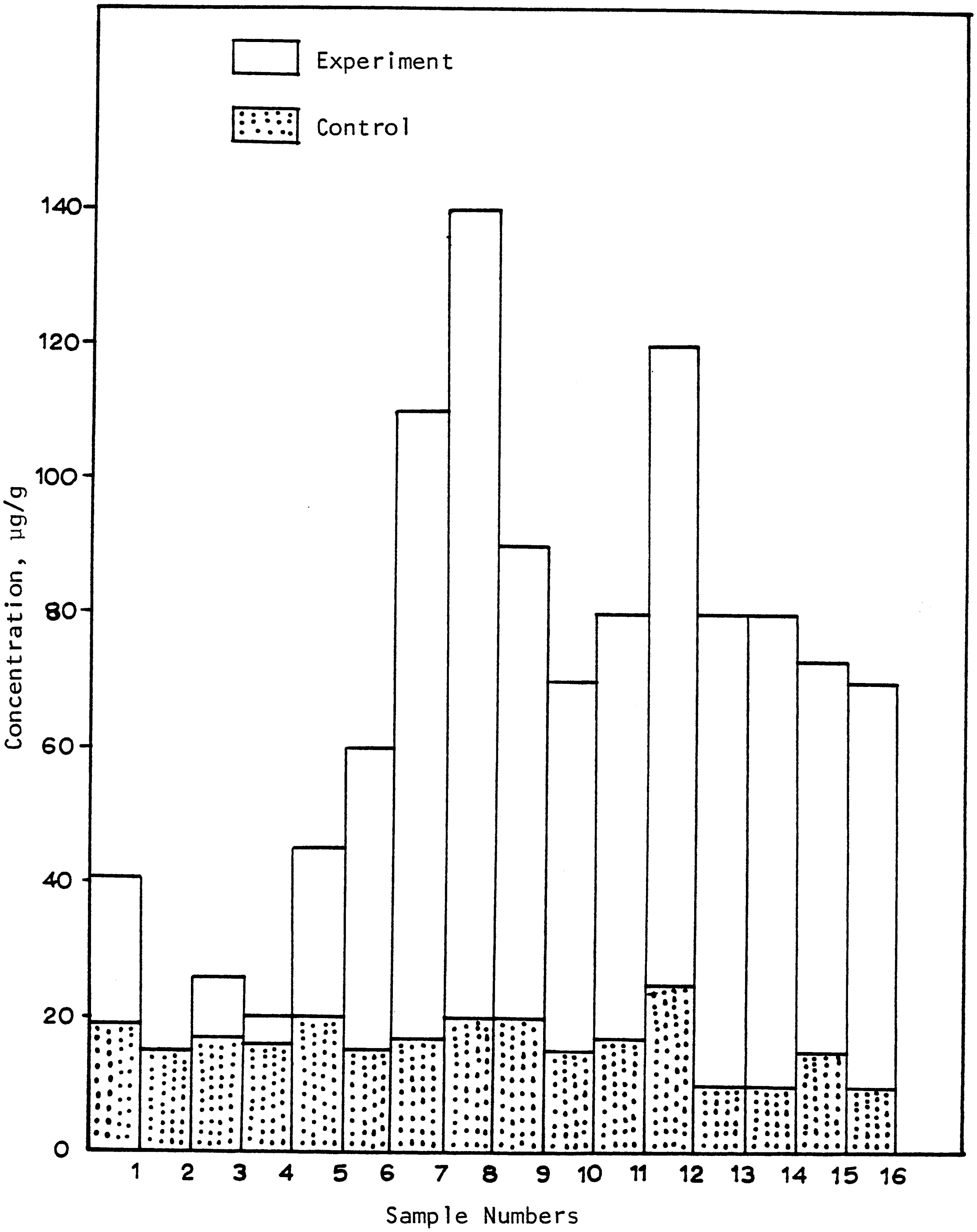

Figure 9. Nickel Concentration in Sediment From Experimental and Control Tanks

Table IX shows the percentages of particulate and dissolved chromium and nickel in water samples. The averages for particulate and dissolved chromium were 76.44% and 23.55% respectively, for nickel, these averages were 33.44% and 66.55% respectively. Those percentages were calculated using sample number 6 through sample number 16 because the dissolved chromium concentration of samples number 1 to 5 were below to detection limit.

The definition of the particulate and dissolved concentrations used in this experiment is just operational. The particulate concentrations were calculated by substraction of the concentrations found in the unfiltered solution from those found in a sample that had been filtered through a 0.45 μ filter.

Tables X to XVII show the average calculated distribution coefficients (Kd) of chromium and nickel in unfilter/filter water, sediment/water, fish/water and fish/sediment. To calculate the distribution coefficients, the graphs of the sorption and desorption phases of both metals were divided arbitrary into stages: early sorption, sample numbers 1 to 6, late sorption, sample numbers 6 to 8, early desorption, sample numbers 8 to 12 and late desorption, sample numbers 12 to 16. The average coefficient distribution was calculated using the following relationships.

$$\text{Kd Unfilter/Filter Water} = \frac{\mu\text{g/L of Cr or Ni Unfilter Water}}{\mu\text{g/L of Cr or Ni Filter Water}}$$

$$\text{Kd Sediment/Water} = \frac{\mu\text{g/Kg of Cr or Ni in Sediment}}{\mu\text{g/L of Cr or Ni in Water}}$$

$$\text{Kd Fish/Water} = \frac{\mu\text{g/Kg of Cr or Ni in Fish}}{\mu\text{g/L of Cr or Ni in Water}}$$

TABLE IX

PERCENTAGES OF PARTICULATE AND DISSOLVED CHROMIUM AND NICKEL IN WATER SAMPLES FROM THE EXPERIMENTAL UNIT

Sample No.	Chromium		Nickel	
	Particulate	Dissolve	Particulate	Dissolve
6	70.00	30.00	42.86	57.14
7	63.64	36.36	30.00	70.00
8	83.33	16.67	33.33	66.67
9	45.00	55.00	48.00	52.00
10	16.67	83.33	25.00	75.00
11	88.89	11.11	33.33	66.67
12	94.38	5.62	40.00	60.00
13	98.50	1.50	25.00	75.00
14	98.50	1.50	23.81	76.19
15	98.67	1.33	32.49	67.51
16	83.33	16.67	34.04	65.96
Average	76.44	23.55	33.44	66.55

TABLE X

DISTRIBUTION COEFFICIENTS (Kd) OF CHROMIUM FOR UNFILTER WATER/FILTER WATER

	Sample Number	Kd
Late Sorption	6 - 8	4.0
Early Sorption	9 - 12	7.5
Late Desorption	13 - 16	49.2

TABLE XI

DISTRIBUTION COEFFICIENTS (Kd) OF NICKEL FOR UNFILTER WATER/FILTER WATER

	Sample Number	Kd
Late Sorption	6 - 8	1.60
Early Desorption	9 - 13	1.55
Late Desorption	14 - 16	1.40

TABLE XII

DISTRIBUTION COEFFICIENTS (Kd) OF CHROMIUM FOR SEDIMENT/WATER

	Sample Number	Kd
Early Sorption	2 - 5	278
Late Sorption	6 - 8	930
Early Desorption	9 - 11	266
Late Desorption	13 - 16	172

TABLE XIII

DISTRIBUTION COEFFICIENTS (Kd) OF NICKEL FOR SEDIMENT/WATER

	Sample Number	Kd
Early Sorption	3 - 6	206
Late Sorption	7 - 8	664
Early Desorption	9 - 11	348
Late Desorption	13 - 16	347

TABLE XIV

DISTRIBUTION COEFFICIENTS (Kd) OF CHROMIUM FOR FISH/WATER

	Sample Number	Kd
Late Sorption	6 - 8	9.71
Early Desorption	9 - 12	3.30
Late Desorption	13 - 16	2.22

TABLE XV

DISTRIBUTION COEFFICIENTS (Kd) OF NICKEL FOR FISH/WATER

	Sample Number	Kd
Late Sorption	4 - 8	6.73
Early Desorption	9 - 11	3.43
Late Desorption	14 - 16	2.06

TABLE XVI

DISTRIBUTION COEFFICIENTS (Kd) OF CHROMIUM FOR FISH/SEDIMENT

	Sample Number	Kd
Late Sorption	4 - 8	193×10^{-4}
Early Desorption	9 - 11	130×10^{-4}
Late Desorption	12 - 16	81×10^{-4}

TABLE XVII

DISTRIBUTION COEFFICIENTS (Kd) OF NICKEL FOR FISH/SEDIMENT

	Sample Number	Kd
Late Sorption	4 - 8	248×10^{-4}
Early Desorption	9 - 11	653×10^{-4}
Late Desorption	14 - 16	63×10^{-4}

$$\text{Kd Fish/Sediment} = \frac{\mu g/gr \text{ of Cr or Ni in Fish}}{\mu g/gr \text{ of Cr or Ni in Sediment}}$$

Those relationships show that the calculated distribution coefficient is dimensionless.

The partitioning coefficient of particulate/dissolved metal was 2.62×10^4 for chromium and 3.6×10^3 for nickel. Those values were calculated using the following formula:

$$\binom{\text{General Partition}}{\text{Coefficient Kpg}} = \frac{\dfrac{[\text{Total Metal } (\mu g/L)] - [\text{Dissolved Metal } (\mu g/L)]}{[\text{Suspended Solids Kg/L}]}}{\text{Dissolved Metal } (\mu g/Kg)}$$

Tables XVIII to XXI show the chromium and nickel concentrations in the control aquarium during the sorption and desorption phases. Chromium concentrations in the water during both phases was always less than 100 μg/L. Sediment concentrations during the sorption phase were in the range of 11 to 20 μg/g, the average concentration was 18 μg/g. The fish concentrations were in the range of 0.17 to 0.70 μg/g and the average concentration was 0.39 μg/g. During the desorption phase (Table XIX), sediment concentrations were in the range of 10 to 30 μg/g, with an average concentration being equal to 16 μg/g. In fish this concentration ranged from 0.34 to 0.98 μg/g with an average of 0.51 μg/g. Sorption and desorption concentrations for nickel are shown in Tables XX and XXI. During part of the sorption phase, nickel concentrations in the water were determined by flame atomic absorption. This technique yielded values always <150 μg/L. In samples analyzed by graphite furnace, during the sorption phase, nickel concentrations ranged from 47 to 150 μg/L, while the average concentration was 127 μg/L. Concentrations in sediment ranged from 15 to 20 μg/g, with

TABLE XVIII

CHROMIUM CONCENTRATION IN CONTROL AQUARIUM DURING SORPTION PHASE

Sample No.	Day	Water (μg/L)	Sediment (μg/g)	Fish (μg/g)
1	5	<100	17	0.50
2	9	<100	16	0.17
3	13	<100	21	0.70
4	17	<100	18	0.24
5	29	<100	20	0.38
6	43	<100	20	0.21
7	55	<100	11	0.53
8	73	<100	20	0.42
Average		<100	18	0.39

TABLE XIX

CHROMIUM CONCENTRATION IN CONTROL AQUARIUM DURING DESORPTION PHASE

Sample No.	Day	Water (μg/L)	Sediment (μg/g)	Fish (μg/g)
9	79	<100	10	0.34
10	83	<100	20	0.25
11	89	<100	20	0.62
12	93	<100	30	0.20
13	97	<100	10	0.65
14	101	<100	10	0.98
15	111	<100	15	0.56
16	125	<100	10	0.48
Average		<100	16	0.51

TABLE XX

NICKEL CONCENTRATION IN CONTROL AQUARIUM DURING SORPTION PHASE

Sample No.	Day	Water (μg/L)	Sediment (μg/g)	Fish (μg/g)
1	5	<150	19	0.36
2	9	<150	15	0.14
3	13	<150	17	0.30
4	17	<150	16	0.13
5	29	47	20	0.12
6	43	150	15	0.07
7	55	110	17	0.36
8	73	110	20	0.20
Average		127	17	0.21

TABLE XXI

NICKEL CONCENTRATION IN CONTROL AQUARIUM DURING DESORPTION PHASE

Sample No.	Day	Water (μg/L)	Sediment (μg/g)	Fish (μg/g)
9	79	140	10	0.17
10	83	110	20	0.21
11	89	120	20	0.33
12	93	90	30	0.16
13	92	80	10	0.33
14	101	110	10	0.78
15	111	35	15	0.10
16	125	95	10	0.22
Average		98	16	0.28

the average concentration being 17 µg/g. In fish the nickel ranged from 0.12 to 0.36 µg/g with an average concentration of 0.21 µg/g (Table XX). During the desorption phase (Table XXI), nickel concentrations in the water ranged from 35.3 to 140 µg/L, with the average concentration being 98 µg/L. In sediment the concentrations were in the range of 10 - 30 µg/g, while the average was 16 µg/g. In fish nickel concentrations ranged from 0.10 to 0.78 µg/g and the average concentration was 0.28 µg/g.

CHAPTER V

DISCUSSION

The concentrations of chromium during the sorption and desorption phases in water, sediment and fish are shown in Tables V and VI. Figures 2, 3 and 4 show the plots of those concentrations. Chromium concentration on day 0 was <100 µg/L, from day 5 to day 43 the chromium concentration was constant at 100 µg/L. Between days 55 and 73 an increase occurred leading to the peak concentration of 120 µg/L on day 73, the last day of this phase. At the beginning of the desorption phase, day 79, the concentration was measured at 200 µg/L which represent an increase of 66% over the concentration in the water on day 73. Between days 101 and 125 an pseudoequilibrium concentration of 300 µg/L was observed. This concentration represented an increase of 150% above the concentration in the water on day 73. The increase in concentration observed is due to the release of metals from sediment and fish. This fact is illustrated by the concentration measured in the sediment on day 73 (last sampling day of sorption) which was 150 µg/g and the concentration measured on day 79 (first sampling day of desorption) 63 µg/g. The drop in metal concentration in the sediment corresponds to a rise in the metal concentration in the water. The sorption of chromium in sediment (Table V, Figure 3) was approximately linear up to a peak concentration of 150 µg/g. Desorption occurred very quickly and on day 79 the concentration was 63 µg/g, a drop of 62% from the concentration on day 73 (Table V). On day 125, the last day of the desorption phase, the concentration was 40 µg/g which represents a decrease of approximately 73%. On day 93, an extremely high concentration was determined, this high concentration was probably due to contamination during sample preparation because the control sediment sample also had a high chromium concentration on day 93 (Table XX, Figure 5). Chromium concentration in fish on day 0 was 0.70 µg/g, from day 5 to day 17 the accumulation of chromium by fish was variable but from day 29 to day 73 a linear increase in the concentration occurred, leading to a peak concentration of 1.40 µg/g on day 73 (Table V, Figure 4) the last day of sorption phase. A low concentration, 0.60 µg/g, was determined on day 17 and which might be related to the small size of the fish taken on that day (Appendix A). The concentrations present in the fish on days 79 and 125 represent a decrease of 43% and 78% respectively from the concentration present in the fish on day 73 (Table VI and Figure 4).

Nickel concentrations in the water during the sorption phase (Table III, Figure 6) were variable from day 5 to day 13. From day 17 to day 43 a linear increase in concentration occurred. But by day 73, end of sorption phase, the concentration had decreased to 180 µg/L. On day 79 the first sampling day of the desorption phase, the water concentration was 250 µg/L which represents an increase of 38% over the concentration on day 73. The sudden decrease in concentration observed in the sediment, between the sampling days 73 and 79, from 140 µg/g to 90 µg/g, respectively, explains again the increase in concentration observed in the water during the desorption phase. Nickel concentration in the sediment on day 0 was 15 µg/g. A fairly linear increase was observed in the nickel accumulation by sediment from day 17 to 73 (Table VII, Figure 7). The maximum nickel concentration accumulated by the sediment was 140 µg/g on day 73. During the desorption phase the nickel concentration in the sediment decreased from 90 μg/g on day 79 to 70 μg/g on day 125. Those concentrations represent a decrease of 35% and 50% respectively from the concentrations present in the sediment on day 73 (Table VII).

Nickel concentration in fish on day 0 was 0.4 μg/g, at the beginning of sorption phase which was day 5 the nickel concentration in the fish was 1.4 μg/g. At the end of this phase between days 55-73, a pseudo-equilibrium concentration of 1.5 μg/g was reached. Again, on day 17 a very low concentration (0.8 μg/g) was observed (Table VII, Figure 8). On day 79, the concentration in the fish was 1.1 μg/g and at the end of this phase, on day 125, it was 0.4 μg/g. Those concentrations represent a drop of 26% and 73% from those present in the fish on day 73 (Table VII).

It is seen from the concentrations of chromium and nickel measured in fish during the sorption phase that the fish Lepomis cyanelus is able to accumulate chromium and nickel at levels much higher than in ambient water and lower than those found in the sediment. According to Murphy et al. 1978 this incorporation of trace metals into fish can occur along two pathways: absorption across the gill surfaces or through the gut tract wall. Mathis and Cummings (1973) found a relationship between trace metal concentrations in fish and the trophic level of the species. Results of their investigation show that higher concentrations of chromium and nickel were present in omnivorous fish than in carnivorous fish. However, Murphy et al. 1978 concluded that regardless of the rate of uptake, metals concentrations in fish are species related.

On the other hand, the gradual decrease in concentration found in fish during desorption phase demonstrates that when the source of pollution is eliminated, chromium and nickel do not persist in biological systems and release of both metals from the fish occurs. In addition, a comparison between the amounts of chromium and nickel determined in the fish and the sediment at the beginning and end of the desorption phase days 79 and 125 respectively, indicate that the desorption of chromium from those compartments was faster than that of nickel. These amounts also show that the desorption of chromium from sediment was also greater than the desorption of nickel. In contrast with these results, Van der Weijden et al. (1977), found in a desorption experiment using 1:1 diluted sea water, the desorption of nickel was greater than the desorption of chromium.

The total input of chromium into the system was 556.6 mg, of which 390.8 mg accumulated in the sediment, 0.622 mg was accumulated by the fish and 167.5 mg stayed in the water. The mass balance resulted in a very good chromium recovery of 101%. For nickel the total input was 569.2 mg, with 493 mg accumulating in the sediment and 0.698 mg accumulating in the fish, while 207.9 mg stayed in the water. The mass balance resulted in a nickel recovery of 136%, which is a little high. It was probably due to the dilutions of the samples which were necessary to overcome some interferences during the analyses of nickel. Another important factor is the fact that this experiment was conducted with real sediment and natural water coming from Lake Carl Blackwell which might have influenced the results because of their competitive reactions with trace metals, solid surfaces and the solution (Hart, 1982).

Results of the percentages of particulate and dissolved chromium and nickel show that chromium was found mainly in the particulate form (76.44%) and nickel was mainly in the dissolved form (66.55%) (Table IX). The results agree with those found by Young et al. (1982) in Onondaga Lake, New York, where 75% of the nickel was in the dissolved form and 75% of the chromium was in the particulate form. Pfiffer (1980), concluded that chromium attached to particles was the main source of chromium transport through the water column in a tributary of the Iraja River, Rio de Janeiro. Perhac (1972), found that in two streams in Tennessee an average of 93.0% of the nickel was on the dissolved solids and 0.12% was on the coarse particles.

Distribution coefficients for chromium and nickel in the unfilter/filter water ratio (Tables X and XI) shows that the distribution coefficient of chromium has a larger value than the distribution coefficient of nickel. This means that chromium tends to be more attached to particulates and nickel tends to be more in solution.

Distribution coefficients of chromium and nickel for the sediment/water ratio in the sorption and desorption phase are shown in Table XII and XIII. These results indicate that both metals, when present in an aquatic ecosystem, tend to go to the sediment. Values of the distribution coefficient of both metals for fish/water during the sorption and desorption phases shows that chromium and nickel tend to be more distributed, or more concentrated, in fish than in water (Table XIV-XV). The distribution coefficients for fish/sediment show that both metals were present in the sediment in higher amounts than in fish during both phases (Table XVI - XVII). When one of the phases of the distribution coefficient is a living organism this coefficient is sometimes called a bioconcentration factor (BCF), the values of distribution coefficients fish/water and fish/sediment may be considered BCF (EPA, 1979).

Tables XXII, XXIII and XXIV compares the results of the distribution coefficients for fish/sediment and sediment/water found in this study with that of the Illinois River which were calculated using data from Mathis

TABLE XXII

DISTRIBUTION COEFFICIENT (Kd) CHROMIUM

Fish Species	Source	Fish/Water	Fish/Sediment
Ictiobus cyprinellus	Illinois River	0.31/0.021 = 14.76	0.13/17 = 76 x 10^{-4}
Dorosoma cepedianum	Illinois River	0.45/0.021 = 21.43	0.45/17 = 265 x 10^{-4}
Moxostoma macrolepidotum	Illinois River	0.09/0.021 = 4.3	0.09/17 = 53 x 10^{-4}
Carpiodes cyprinus	Illinois River	0.21/0.021 = 10	0.21/17 = 123 x 10^{-4}
Cyprinus carpio	Illinois River	0.16/0.021 = 7.6	0.16/17 = 94 x 10^{-4}
Lepomis cyanelus	This Study	1040/106 = 9.8	0.04/75.06 = 138 x 10^{-4}

TABLE XXIII

DISTRIBUTION COEFFICIENT (Kd) NICKEL

Fish Species	Source	Fish/Water	Fish/Sediment
Ictiobus cyprinellus	Illinois River	0.10/0.002 = 50	0.10/27 = 37×10^{-4}
Dorosoma cepedianum	Illinois River	0.28/0.002 = 140	0.28/27 = 103×10^{-4}
Moxostoma macrolepidotum	Illinois River	0.14/0.002 = 70	0.14/27 = 51×10^{-4}
Carpiodes cyprinus	Illinois River	0.18/0.002 = 90	0.18/27 = 67×10^{-4}
Cyprinus carpio	Illinois River	0.56/0.002 = 280	0.56/27 = 207×10^{-4}
Lepomis cyanelus	This Study	1280/190 = 673	1.33/78.6 = 169×10^{-4}

TABLE XXIV

DISTRIBUTION COEFFICIENT (Kd) SEDIMENT/WATER

Source	Chromium	Nickel
Illinois River	17/0.021 = 809.5	27/0.002 = 13500
This Study	60600/104.42 = 580.3	66800/780 = 377

NOTE: The distribution coefficients from the data in this study were calculated using the average metal concentration in each step for the sorption phase.

and Cummings (1973). It is seen from this comparison that chromium and nickel in both studies show the same distribution trends.

The general partitioning coefficient of particulate to dissolved metal (Kpg) for chromium, 2.62×10^4, was higher than the Kpg value for nickel, 3.6×10^3. This illustrates the trend of chromium to stay in a particulate form and nickel in dissolved form. The Kpg for chromium was of the same order of magnitude as that reported by EPA (1984), for copper in Lake Huron; the Kpg for copper was in the range of 10^4 - 10^5.

These results suggest that the chromium in Lake Carl Blackwell remains attached to particles and that nickel stays in the dissolved form. Various sources confirm that chromium and nickel in natural aquatic systems follow the same behavior as that observed in this research (Perhac, 1972; Gibbs, 1973; Nriagu, 1980; and Young et al., 1982).

Tables XVIII and XIX shows the chromium concentrations in the water, sediment and fish from the control tank during the sorption and desorption phases. Chromium concentrations in water was always below the detection limit of Flame Atomic Absorption, 100 µg/L. In sediment the average concentration during the sorption phase and desorption phase were 18 µg/g and 16 µg/g respectively, in fish those average concentrations were 0.39 µg/g and 0.51 µg/g respectively. The average concentration of nickel in water during the sorption and desorption phases (Tables XX - XXI), were 127 µg/L and 98 µg/L respectively. In sediment those average were 17 µg/g and 16 µg/g respectively while in the fish they were 0.21 µg/g and 0.28 µg/g respectively. Concentrations of chromium and nickel present in the control aquarium may be considered of natural origin because Lake Carl Blackwell does not receive any industrial or municipal effluents.

Howick et al. 1982 reported 0.16 g/m^3 of chromium released from Lake Carl Blackwell sediments by elutriation and also concentrations in fish in the range of not detected for white bass to 23.4 μg/g for carp.

The calculated distribution coefficients between the various compartments of the simulated aquatic ecosystem helps fill a void in the current literature. Partitioning or distribution coefficients for organics are fairly common while the same coefficients for heavy metals are not. The kd's attained at equilibrium, or pseudo-equilibrium, the end of the sorption phase and end of desorption phase could be used in simple models to help verify the models ability to predict the distribution of nickel and chromium in an aquatic ecosystem. The desorption kd's could be used to help predict the distribution of metals following an event of metal pollution. A simple completely mixed compartment model with advection and sediment interaction could be used to describe this system.

CHAPTER VI

CONCLUSIONS

The sediment accumulated the highest concentration of chromium and nickel during the sorption step of any phase. The amounts of chromium and nickel determined at the beginning and at the end of the desorption phase showed that the desorption of chromium from the sediment was faster and to a greater extent than the desorption of nickel.

The fish species Leponus cyanellus used in this investigation is able to accumulate chromium and nickel at levels higher than its surrounding ambient water. The decrease in metals concentrations determined in the fish during the desorption phase showed that chromium and nickel did not stay in the fish when the addition of metal to the system ceased.

As showed in this study the Distribution Coefficients of both metals for unfilter water/filter water, and the partitioning coefficient for perticulated/dissolved metal, as well as the percentages of particulate and dissolved chromium and nickel, suggest that chromium remains attached to particles and nickel remains in solution in the Lake Carl Blackwell.

The distribution coefficients values of chromium and nickel for sediment/water, fish/water and fish/sediment during the sorption and desorption phases demonstrated that both metals tend to be more distributed or concentrated in the sediment and in the fish than in the water.

CHAPTER VII

RECOMMENDATIONS

1. In future studies, use at least two different fish species and a few aquatic plants to compare the metal accumulation by species.

2. Determine the total organic carbon and mean grain size of the sediment in order to know the correlation between sorption capacity of the sediment and those parameters.

3. Examine the clay mineralogy and its effects in sorption of chromium and nickel.

4. Determine the iron and manganese content of the water and sediment to know the correlation between sorption of chromium and nickel and concentration of those metals.

5. Collect a greater number of samples so that any sorption or desorption point may be statistically represented.

BIBLIOGRAPHY

1. Ajmal, M. and A. V. Khan. 1984. Effect of water hardness on the toxicity of cadmium to micro-organisms. Water Res. 18(12):1487-1491.

2. Angino, E. E., L. M. Magnuson and T. C. Waugh. 1974. Mineralogy of suspended sediment and concentration of Fe, Mn, Ni, Zn, Cu and Pb in water and Fe, Mn, and Pb in suspended load of selected Kansas streams. Water Res. 10(6):1187-1191.

3. Baptist, J. P. and C. W. Lewis. 1969. Transfer of ^{65}Zn and ^{51}Cr through an estuarine food chain. pp. 420-430. Proc. 2nd Nat. Symp. on Radioecology. U.S. Atomic Energy Commission Conf. 670503. 631 p.

4. Becker, C. D. and M. G. Walford. 1980. Thermal resistance of juvenile salmonids sublethally exposed to nickel, determined by the critical thermal maximum method. Environmental Pollution (Series A) 21:181-190.

5. Benoit, D. A. 1976. Toxic effects of hexavalent chromium on brout trout (Salvelinus fontinalis) and rainbow trout (Salmo gairdneri). Water Res. 10:497-500.

6. Bradford, G. R., F. L. Bair and V. Hunsake. 1968. Trace and major element content of 170 High Sierra Lakes in California. Limnol. Oceanogr. 13, 526-529.

7. Brooks, R. R. and D. Rumsey. 1974. Heavy metals in some New Zealand commercial sea fishes. New Zealand Journal of Marine and Freshwater Research 8:155-166.

8. Durum, W. H., and Haffty, J. 1963. Implications of the minor element content of some major streams of the world. Geochim. Cosmochim. Acta. 27:1-11.

9. Environmental Protection Agency (EPA). 1979. Water-related environmental fate of 129 priority pollutants. Volume 1: Introduction and technical background, metals and inorganics, pesticides and PCBs. Office of Water Planning and Standards. Office of Water and Waste Management, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/4-79-0292.

10. Environmental Protection Agency (EPA). 1983. Methods of Chemical Analyses of Water and Wastes. U.S. Environmental Protection Agency, Off. of Tech. Transfer, Cincinnati, OH. EPA-600/4-79-023.

11. Environmental Protection Agency (EPA). 1984. Partitioning of toxic trace metals between solids and liquid phases in the Great Lakes. U.S. Environmental Protection Agency, Off. of Res. and Develop. Duluth, MN. EPA-600/D-84-098.

12. Friant, S. L. 1979. Trace metal concentrations in selected biological, sediment, and water column samples in a northern New England River Water, Air and Soil Poll. 11:455-465.

13. Friedrich, A. R. and F. P. Filice. 1976. Uptake and accumulation of the nickel ion by Mytilus edulis. Bull. Environ. Cotam. Toxicol. 16(6):750-759.

14. Gibbs, R. J. 1973. Mechanisms of trace metal transport in rivers. Science 180, 71-73.

15. Griffin, R. A., A. K. Au, and R. R. Frost. 1977. Effect of pH on adsorption of chromium from landfill-leachate by clay minerals. J. Environ. Sci. Health A12(8):431-449.

16. Hart, H. T. 1982. Uptake of trace metals by sediments and suspended particulates. A review. Hydrobiologia 91:299-313.

17. Howick, G. L., J. L., Wilhm, D. L., Toetz and S. L. Burks. 1982. Diagnostic study of Lake Carl Blackwell, Department of Zoology, Oklahoma State University.

18. Hughes, G. M. and S. F. Perry. 1979. A morphometric study of effects of nickel, chromium and cadmium on the secondary Lamellae of Rainbow Trout gills. Water Res. 13:665-679.

19. Jackson, K. S. and G. B. Skippen. 1978. Geochemical dispersion of heavy metals via organic complexing: A laboratory study of copper, lead, zinc and nickel behavior at a simulated sediment-water boundary. Journal Geoch. Explo. 10:117-138.

20. Krishnamurty, K. V., E. Shirt, and Reddy, M. M. 1976. Trace metal extraction of soils and sediments by nitric acid-hydrogen peroxide. Atomic Abs. Newsletter. 15(3):68-70.

21. Leonard, E. N. 1971. The determination of copper in fish tissues by Atomic Absorption Spectrophotometry. Atomic Abs. Newsletter. 10(4)84-85.

22. Mathis, B. J. and T. F. Cummings. 1973. Selected metals in sediments, water, and biota in the Illinois River. J. Water Poll. Control Fed. 45(7):1573-1582.

23. McKee, J. E. and H. W. Wolf. 1963. Water Quality Criteria, 2nd ed. State Water Quality Control Board, Sacramento, Calif., 548 pp.

24. Mearns, A. J., P. S. Oshida, M. J. Sherwood, D. R. Young, and D. J. Reish. 1976. Chromium effects on coastal organisms. J. Water Poll. Contro Fed. 48(8): 1929-1939.

25. Moore, J. W., and S. Ramamoorthy. 1984. Heavy metals in natural waters. Applied Monitoring and Impact Assessment. Springer-Verlag, New York, Berlin Heidelberg, Tokyo, pp. 62-76.

26. Muramoto, S. 1981. Influence of complexans (NTA, EDTA) on the toxicity of trivalent chromium (chromium chloride, sulfate) at levels lethal to fish. J. Environ. Sci. Health, 6:605-610.

27. Muramoto, S. 1983. Influence of complexans (NTA, EDTA) on the toxicity of nickel chloride and sulfate to fish at high concentrations. J. Environ. Sci. Health, A18(6):787-795.

28. Murphy, B. R., G. J. Atchison and A. W. McIntosh. 1978. Cadmium and zinc content of fish fr-m an industrially contaminated lake. J. Fish. Biol. 13:327-335.

29. Namminga, H. and J. Wilhm. 1977. Heavy metals in water, sediments and chironomids. Jour. Water Poll. Control Fed., 1725-1729.

30. Nriagu, J. O. 1980. Nickel in the Environment, Wiley, New York.

31. Perhac, R. M. 1972. Distribution of Cd, Co, Cu, Fe, Mn, Ni, Pb and Zn in dissolved and particulate solids from two streams in Tennessee. Journal of Hydrology, 15:177-186.

32. Pfeiffer, W. C., M. Fiszman and N. Carbonell. 1980. Fate of chromium in a tributary of the Iraja River, Rio de Janeiro. Environ. Poll. Ser. B 1:127-148.

33. Pickering, Q. H., and C. Henderson. 1966. The acute toxicity of some heavy metals to differents species of warmwater fishes. Air Wat. Pollut. Int. J. 10:453-463.

34. Pickering, Q. H. 1974. Chronic toxicity of nickel to the fathead minnow. J. Water Pollut. Control Fed. 46:760-765.

35. Pickering, Q. H. 1980. Chronic toxicity of hexavalent chromium to the fathead minnow (Pimephales promelas). Arch. Environm. Contam. Toxical. 9:405-413.

36. Rehwoldt, R., Bida, G., and Nerrie, B. 1971. Acute toxicity of copper, nickel and zinc ions to some Hudson River fish species. Bull. Environ. Contam. Toxicol., 10(5):291-294.

37. Shcroeder, D. C. and G. F. Lee. 1975. Potential transformations of chromium in natural waters. Water, Air and Soil Poll. 4:355-365.

38. Smith, M. J., and A. G. Heath. 1979. Acute toxicity of copper, chromate, zinc, and cyanide to freshwater fish; effect of different temperatures. Bulletin of Environmental Contamination and Toxicology 22:113-119.

39. Steele, K. F. and G. H. Wagner. 1975. Trace metal relationships in bottom sediments of a fresh water stream--the Buffalo River, Arkansas. J. Sed. Petrol. 45(1):310-319.

40. Taylor, M. C., S. T. Reeder and A. Demayo. 1979. Guidelines for surface water quality. Vol. 1. Inorganic chemical substances. Inland waters directorate, water quality branch, Ottawa, Canada. 3 p.

41. Van Der Putte, I., M. A. Brinkhorst, and J. H. Koeman. 1981. Effect of pH on the acute toxicity of hexavalent chromium to rainbow (Salmo gairdneri). Aquatic Toxicology 1:129-142.

42. Van Der Weijden, C. H., M. J. H. L. Arnoldus and C. J. Meurs. 1977. Desorption of metals from suspended material in the Rhine estuary. Nether. J. Sea. Res. 11(2):130-145.

43. Young, T. C., J. V. De Pinto and E. S. Seger. 1982. Transport and fate of heavy metals in Onondaga Lake, New York. Bull. Environm. Contam. Toxicol. 29:554-561.

APPENDIX A

FISH SAMPLES FOR EXPERIMENTAL AND CONTROL TANKS

TABLE XXV

FISH SAMPLES FOR EXPERIMENTAL TANK

Sample No.	Sample Date	Length (cm)	Height (cm)	Weight (g)
1	8/11/84	15.0	5.5	65.1940
2	8/11/84	13.5	5.0	46.3676
3	8/11/84	12.0	4.0	32.5767
4	8/15/84	13.0	4.5	40.1802
5	8/19/84	14.0	3.5	43.8402
6	8/23/84	12.0	3.5	29.3190
7	8/23/84	10.0	3.5	20.8600
8	9/04/84	14.0	5.0	48.7805
9	9/18/84	12.0	4.0	28.9986
10	9/30/84	13.5	5.0	46.1990
11	10/18/84	12.0	4.0	29.7120
12	10/24/84	14.5	5.0	61.6226
13	10/28/84	11.5	3.5	24.1870
14	11/03/84	11.0	3.5	20.8370
15	11/03/84	13.0	4.5	46.9448
16	11/07/84	13.0	5.0	31.5766
17	11/11/84	15.4	5.0	63.4815
18	11/15/84	15.0	5.0	74.5392
19	11/25/84	18.0	6.5	109.7880
20	11/25/84	15.0	5.5	70.4826
21	11/25/84	15.0	5.0	40.5075
22	12/09/84	12.5	4.0	25.5362
23	12/09/84	15.0	5.5	66.9224

TABLE XXVI

FISH SAMPLES FOR CONTROL TANK

Sample No.	Sample Date	Length (cm)	Height (cm)	Weight (g)
1	8/11/84	15.0	5.5	81.5720
2	8/11/84	15.0	5.0	66.2883
3	8/11/84	13.0	4.5	52.0360
4	8/15/84	10.5	4.5	19.6898
5	8/19/84	13.0	4.5	42.1802
6	8/23/84	13.5	4.5	42.3051
7	8/23/84	10.0	4.0	22.7500
8	9/4/84	12.0	4.0	30.6938
9	9/18/84	13.0	4.0	27.8566
10	9/30/84	10.5	4.0	22.3518
11	10/18/84	16.0	6.0	91.3780
12	10/24/84	12.5	4.0	35.0253
13	10/28/84	13.0	5.0	41.4520
14	11/3/84	13.0	4.5	39.7912
15	11/3/84	14.0	5.0	44.5198
16	11/7/84	10.5	4.3	29.0129
17	11/11/84	13.5	4.5	28.8257
18	11/15/84	14.5	5.5	61.8451
19	11/25/84	15.0	5.5	75.2256
20	11/25/84	12.5	3.5	37.9732
21	11/25/84	15.5	5.5	65.3540
22	12/9/84	13.0	5.0	45.5380
23	12/9/84	14.5	5.0	50.0360

APPENDIX B

EXAMPLE SHOWING THE CONVERSION OF DRY WEIGHT TO WET WEIGHT

Fish No. 5

Weight: 43.8402 g

Volume of water added: 40 ml

Subsample weight: 78.3229 g

Total Weight: 43.8402 + 40 = 83.8402 g

$$\frac{40}{83.8402} = 47.7\% \text{ of } H_2O$$

78.3229 g x 0.477 = 3736 g

78.3229 g - 37.36 g = 40.96 g Wet Weight

Dry Weight: 9.8533 g

Conversion of nickel concentration in dry weight to nickel

Concentration in wet weight

$$\frac{\text{mg/L in Solution} \times 0.01\text{L}}{\text{Sample Dry Weight(g)} \left(\frac{\text{Wet Weight (g)}}{\text{Dry Weight (g)}}\right)} = \text{mg/g of Metal in Sample}$$

$$\frac{0.15 \text{ mg/L} \times 0.01\text{L}}{0.25 \text{ g} \times \left(\frac{40.96 \text{ g}}{9.8533 \text{ g}}\right)} = 0.00144 \text{ mg/g} = 1.44\ \mu\text{g/g}$$

Total nickel concentration in the fish.

Concentration in the sample x (Weight of Fish).

1.44 μg/g x (43.8402 g) = 63.13 μg.

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