CHARACTERIZATION OF HEAVY METAL CONCENTRATIONS
IN THE
MAHONING RIVER BOTTOM SEDIMENTS

by

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ABSTRACT

CHARACTERIZATION OF HEAVY METAL CONCENTRATIONS IN THE MAHONING RIVER BOTTOM SEDIMENTS

Over the past ten years, a decrease in heavy metal loadings to the Mahoning River has occurred. Due to the closing of several steel mills and stringent effluent limitations being imposed on discharge sources, the Mahoning is expected to show a slow recovery, in which heavy metal levels in the river bottom sediments will decrease.

Variations in heavy metal concentrations with depth and length along the course of the Mahoning River were investigated in this study. Grab samples and core samples of river sediment were taken, air dried, pulverized, and digested, then analyzed with flame Atomic Absorption analysis. The metals analyzed were cadmium, chromium, copper, iron, lead, manganese, nickel and zinc.

Based on the data generated, a consistent trend was noticed in the sediment metal concentrations as a function of river mile. The overall tendency was for the metal levels to increase dramatically at the beginning of the industrialized section of the river. Following the initial spike, there was a net decrease in metal levels the closer to the river's mouth the samples were taken. As for variation with sediment depth,

ABSTRACT (cont.)

it was difficult to distinguish a consistent trend for the entire river. Even at the individual coring locations, heavy metal profiles varied along the channel cross section. Based on the data collected for the core samples taken across the river channel, the metal concentrations in the river sediments showed increasing concentrations, decreasing concentrations and no distinct trend in metal concentrations varying with depth.

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CHAPTER 1

INTRODUCTION

History of the Mahoning River

The Mahoning River extends for approximately 108 miles from its conception at the Berlin Reservoir to where it joins the Shenango River in New Castle, Pennsylvania. The Mahoning River has a drainage basin covering approximately 1133 square miles as shown in Figure 1.1. Various reservoirs built to serve the Mahoning provide low flow augmentation and temperature control, while low head channel dams along the course of the river provide water supply and flood control (1). During the late 1960's and early 1970's, the Mahoning River was heavily exploited by industrial dischargers and municipal wastewater dischargers using mostly primary treatment for solids removal. Figure 1.2 shows the locations of various industrial dischargers, municipal wastewater dischargers and a coal-fired power plant which exploited the resources of the river. Additional municipal and industrial dischargers are also located on the adjoining tributaries which contribute to the flow of the river. Historically, the water quality in the river was characterized by high temperatures, low dissolved oxygen, high levels of ammonia-N, and elevated heavy metal concentrations as a direct result of discharge from industries along the river's banks. Another

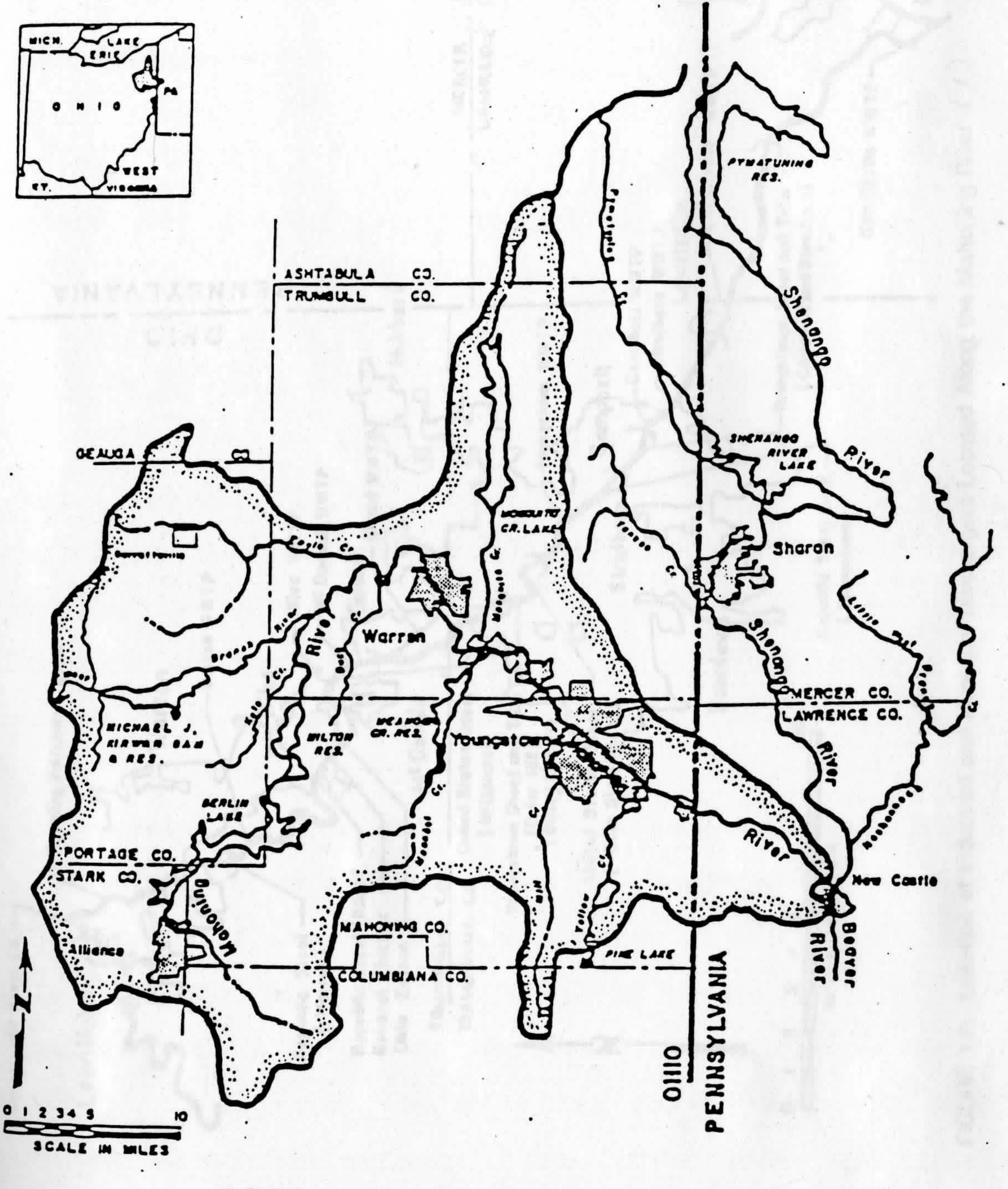


FIGURE 1.1: Drainage Basin Area of The Mahoning River (1)

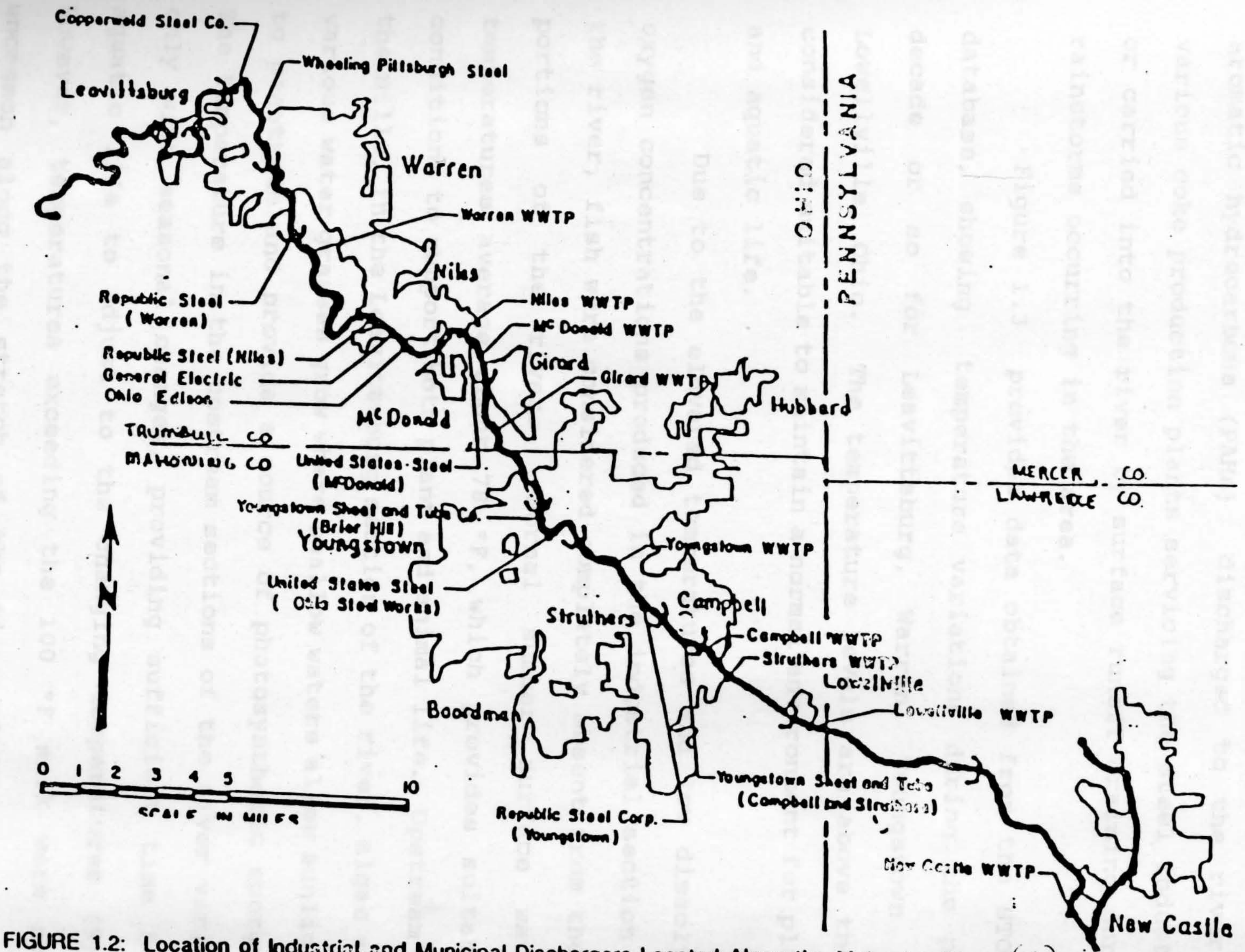


FIGURE 1.2: Location of Industrial and Municipal Dischargers Located Along the Mahoning River (1)

contributing factor was the excessive amount of polynuclear aromatic hydrocarbons (PAHs) discharged to the river by various coke production plants servicing the steel industry, or carried into the river by surface runoff draining during rainstorms occurring in the area.

Figure 1.3 provides data obtained from the STORET database, showing temperature variations during the past decade or so for Leavittsburg, Warren, Youngstown and Lowellville, Ohio. The temperature levels are above those considered suitable to maintain a normal environment for plant and aquatic life.

Due to the elevated temperatures and low dissolved oxygen concentrations produced in the industrial section of the river, fish were considered completely absent from these portions of the river. Normal summer surface water temperatures average about 78 °F, which provides suitable conditions to support both plant and animal life. Upstream of the mills, in the Leavittsburg section of the river, algae and various water grasses grow where shallow waters allow sunlight to penetrate and provide a source of photosynthetic energy. The temperature in the upstream sections of the river varied only with seasonal changes, providing sufficient time for aquatic life to adjust to the changing temperatures (9). However, temperatures exceeding the 100 °F mark were not uncommon along the stretch of the river where the steel industries discharged waters used for cooling processes

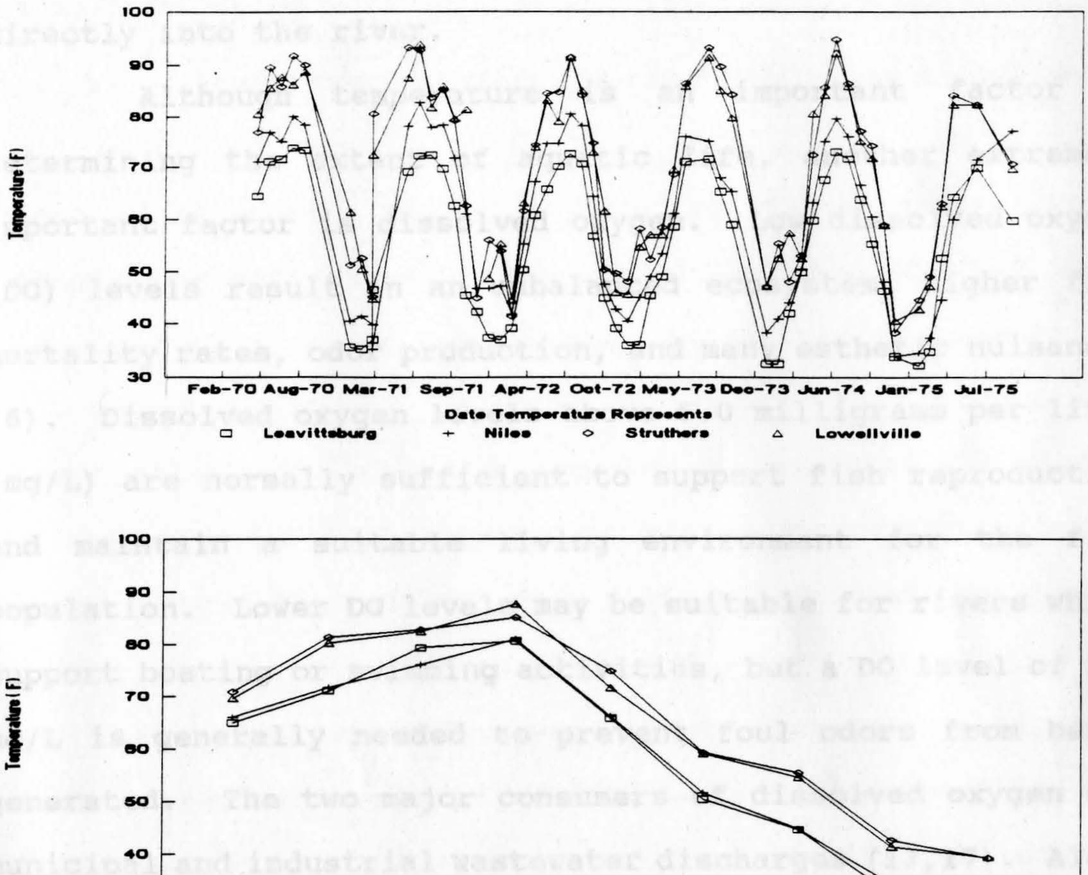


FIGURE 1.3: Temperature Variations in the Mahoning River at Leavittsburgh, Niles, Struthers and Lowellville, Ohio

directly into the river.

Although temperature is an important factor in determining the extent of aquatic life, another extremely important factor is dissolved oxygen. Low dissolved oxygen (DO) levels result in an unbalanced ecosystem, higher fish mortality rates, odor production, and many esthetic nuisances (6). Dissolved oxygen levels above 5.0 milligrams per liter (mg/L) are normally sufficient to support fish reproduction and maintain a suitable living environment for the fish population. Lower DO levels may be suitable for rivers which support boating or swimming activities, but a DO level of 2.0 mg/L is generally needed to prevent foul odors from being generated. The two major consumers of dissolved oxygen are municipal and industrial wastewater discharges (13,17). Along the banks of the Mahoning, there are numerous municipal and industrial sources which discharge to the river directly or through one of the adjoining tributaries. Oxidation of carbonaceous and nitrogenous waste material along with sediment oxygen demand and oxygen used by aquatic plants for respiration also contribute to consumption of DO in river waters.

Water temperature also has a direct impact on the DO levels found in various receiving waters. As temperatures increase in a receiving water, the saturation concentration and actual concentration of dissolved oxygen decrease. At 32 °F, the saturation concentration for oxygen in water is

14.6 mg/l and at 86^{o}F, the oxygen saturation concentration is 7.6 mg/l (13). Temperatures exceeding 100 °F were not uncommon in the industrial section of the river, and saturation concentrations of 6.4 mg/l are typical for these temperatures. Although the saturation values are higher than the 5.0 mg/l concentration previously discussed, the actual concentration in a surface water is usually below the saturation concentration. The elevated temperatures reportedly produced foul odors which would continually rise during the summer months. Upstream of Warren's industrial district, more abundant populations of both plant and aquatic life exist.

Many greases, oils, and solvents were in use in the numerous industrial plants dealing with various metals and metal fabrication processes. As the result of direct discharge or possible surface runoff, the river was subjected to polynuclear aromatic hydrocarbon (PAH) loadings, as well as large quantities of both dissolved metals and metal shavings discharged to the river. The presence of the PAHs and heavy metals within the river bottom sediments present a toxic environment for plants, animal or man coming in contact with the river and its sediments. The fish located along the banks of the Mahoning are the most susceptible to the toxic effects from the sediments since they are mostly bottom feeding species (9).

Current Status

As the steel mills began to close in the late 1970's, As the steel mills began to close in the late 1970's, the plant and fish population began to show a slow increase in numbers and eventually spread into portions of the river where they previously did not exist. Along with the increasing appearance of various fish species, small crawfish and frogs also began to slowly migrate into the areas of the river where they previously did not exist. The fish life within the Mahoning presently consists of carp, channel catfish, and small bass. Fish spotted in the industrialized section of the river during the industrial boom of the steel mills were mostly fish-kill. Upstream of Leavittsburg, the river was, and still is, used as a source of recreation for boating, swimming and fishing. The Health Department recently published a health advisory against consuming fish or swimming in the Mahoning, due to elevated levels of PAHs still present in the the bottom sediments (18).

With the recent improvement in water quality in the Warren-Youngstown stretch of the river, increased interest in recreational use of the river has developed. Water quality data indicates improvements in the water column parameters of temperature, D.O. levels, and lower heavy metals concentrations. But, the quality of the bottom sediments is expected to recover at a much slower rate. Recent data indicate that the sediments still contain high levels of heavy metals and PAHs (14,15).

Objective of Study

current levels of heavy metals in the bottom sediments, specifically iron, copper, cadmium, chromium, lead, zinc, nickel, aluminum, and manganese. Core and grab samples of sediment were taken for the purpose of determining variation of metal concentrations with depth, width and length within the river channel. Variations in heavy metal concentrations with depth in the cores were used to determine if the loading reductions are resulting in reduced concentrations in the river sediment. The cross-sectional cores were used to suggest whether the banks or the center channel of the river are more prone to metal accumulation. The grab samples were used to determine how metal concentrations vary along the length of the river, and possible locations that are still subjected to metal loadings.

There are known discharge sources of heavy metals which still exist along the course of the river. Ideally, we would like to know what sediment metal concentrations to expect under the present loadings after the river has reached steady state. The results of this study almost certainly reflect the effects of past loadings to a major extent. To predict what heavy metal concentrations should be expected under different loading rates, a mathematical model of metals in the river must be applied. Due to the extent of the sampling conducted on the river sediments, a substantial data base was developed in this study. This information could be used in applying mathematical models to aid in predicting what the Mahoning River's future might hold.

CHAPTER II

LITERATURE REVIEW

Metals Accumulation and Distribution in the Food Chain

Heavy metals deposited within the Mahoning River pose a threat to both the plant and aquatic life within the river as well as the plant and animal life living on the river banks. Once discharged into the river, heavy metals do not settle directly to the river bottom and remain locked away in the bottom sediments forever. Once the metals enter the river environment, they are distributed throughout the entire river ecosystem. The organisms typically found in a river ecosystem are of the following four classifications: 1) Saprophytes that live off dead or decaying organic matter; 2) Chemoautotrophs that obtain energy from oxidation of inorganic chemicals and carbon from CO_2; 3) Chemophototrophs that use light as a source of energy; and 4) Predators that live off other living organisms. Saprophytic organisms consume dead organic material which is in contact with the water column and contaminated bottom sediments. The autotrophs obtain their energy from the sun, and food supply from the water body and sediments in which they are rooted. Predators in turn consume saprophytic organisms, autotrophs and small predators. All organisms die and are consumed by the saprophytic organisms (17). Thus the heavy metals present in the food chain of the river are passed on through the entire system. Man would be classified as a predator and would consume the predators living within the river and possibly some of the autotrophic organisms. Man helps to carry the food chain one step further by consuming a food supply which may be contaminated with higher levels of metals.

Health Effects of Heavy Metals

Concentrations at which the metals are found within the food supply or ecosystem are extremely important to whether they are deemed harmful or not. At some concentration, all chemicals known to man can prove harmful to human life (3). Although some are more well known due to the lower concentrations at which they may produce detrimental health effects, all metals need to be considered for possible toxicity to the human race. The metals which are known to pose a serious threat to human health when present in drinking water are regulated through the USEPA Primary Drinking Water Standards. These regulated metals must be maintained below a certain maximum contaminant level (or MCL) to prevent harm to the general public using the drinking water.

Table 2.1 shows three of the metals which are regulated in the Primary Drinking Water Standards and covered by the scope of this study. Both the maximum contaminant levels (MCL) and various related health effects are listed. These three metals are regulated by the Federal Environmental

TABLE 2.1

REGULATED METALS UNDER THE PRIMARY DRINKING WATER STANDARDS (17).

CONSTITUENT	HEALTH EFFECT	MCL (mg/L)
Cadmium	Long-term - concentrates in the liver, kidneys, pancreas and thyroid; hypertension suspected effect	0.01
Chromium	Long-term - skin sensitization and kidney damage, cancer of respiratory and gastrointestinal tract	0.05
Lead	Long-term - brain and kidney damage; birth defects, also affect gastrointestinal tract and reproductive system	0.05

Protection Agency due to the known toxic effects associated with them. The remaining five metals encompassed in the scope of the study also pose some serious health affects to humans, but these metals are not regulated at the present time.

Table 2.2 summarizes potential health effects of the remaining metals measured in this study which are not covered by the Primary Drinking Water Standards. The metals levels in surface waters are controlled by enforcing discharge permit restrictions on municipal and industrial dischargers. The EPA limits the amount of metals these dischargers are allowed to load to a river without creating an environment which may prove unsafe to both aquatic and human life. The Federal EPA has established a list of toxic substances which any discharge

TABLE 2.2

POTENTIAL HEALTH EFFECTS OF METALS INCLUDED IN THIS STUDY BUT NOT COVERED BY THE PRIMARY DRINKING WATER STANDARDS (17)

Copper	Long-term - affects central nervous system, liver, kidney and cornea
Nickel	Long-term - respiratory tract carcinogen, allergic contact dermatitis
Iron	Long-term - liver disturbance, diabetes mellitus, effect cardio-vascular system
Zinc	Long-term - gastrointestinal distress and diarrhea

source must monitor and produce effluent concentrations below levels set by state EPA. This list is called the Priority Toxic Water Pollutants (12).

Of the metals covered by the scope of this study, cadmium (total), chromium (total), copper (total), lead (total), nickel (total) and zinc (total) are included on the priority list (17).

Processes Affecting Heavy Metals Distribution in Rivers

Dischargers are a very important factor influencing metals loadings entering a river. The industrial discharges from metal processing plants and the cooling waters generated by various production processes used by the steel mills are only two of the numerous contamination sources along the Mahoning River. Surface runoff from scrap yards and municipal wastewater discharges also contribute to the total metal loadings to the river. The locations of various industries and municipal wastewater dischargers located along the course of the Mahoning River were shown in Figure 1.2.

The metals entering a river may be found in two forms-dissolved metals and metals attached to particulate matter. The processes which directly affect the distribution of metals, both in the water column and bottom sediments, are shown schematically in Figure 2.1.

Adsorption occurs in the water column when a dissolved metal ion with a positive charge passes in the direct vicinity of a negatively charged site on the surface of a suspended particle. Due to the difference in charge, the dissolved metal and suspended particle have an affinity for each other. In addition to the electrostatic or physical adsorption, metal ions may be chemically adsorbed by forming covalent bonds with functional groups on the particle surface. Desorption results when the electrostatic attraction decreases or the covalent bond is broken forcing the metal ions back into solution. The adsorption/desorption processes also occur between the layered sediments and interstitial water which exist within the bottom sediments.

Diffusion is another important process which affects the distribution of dissolved metal ions. When a concentration gradient exists between two regions, such as the water column and interstitial water in the bottom sediments, there is a natural tendency for the constituent experiencing

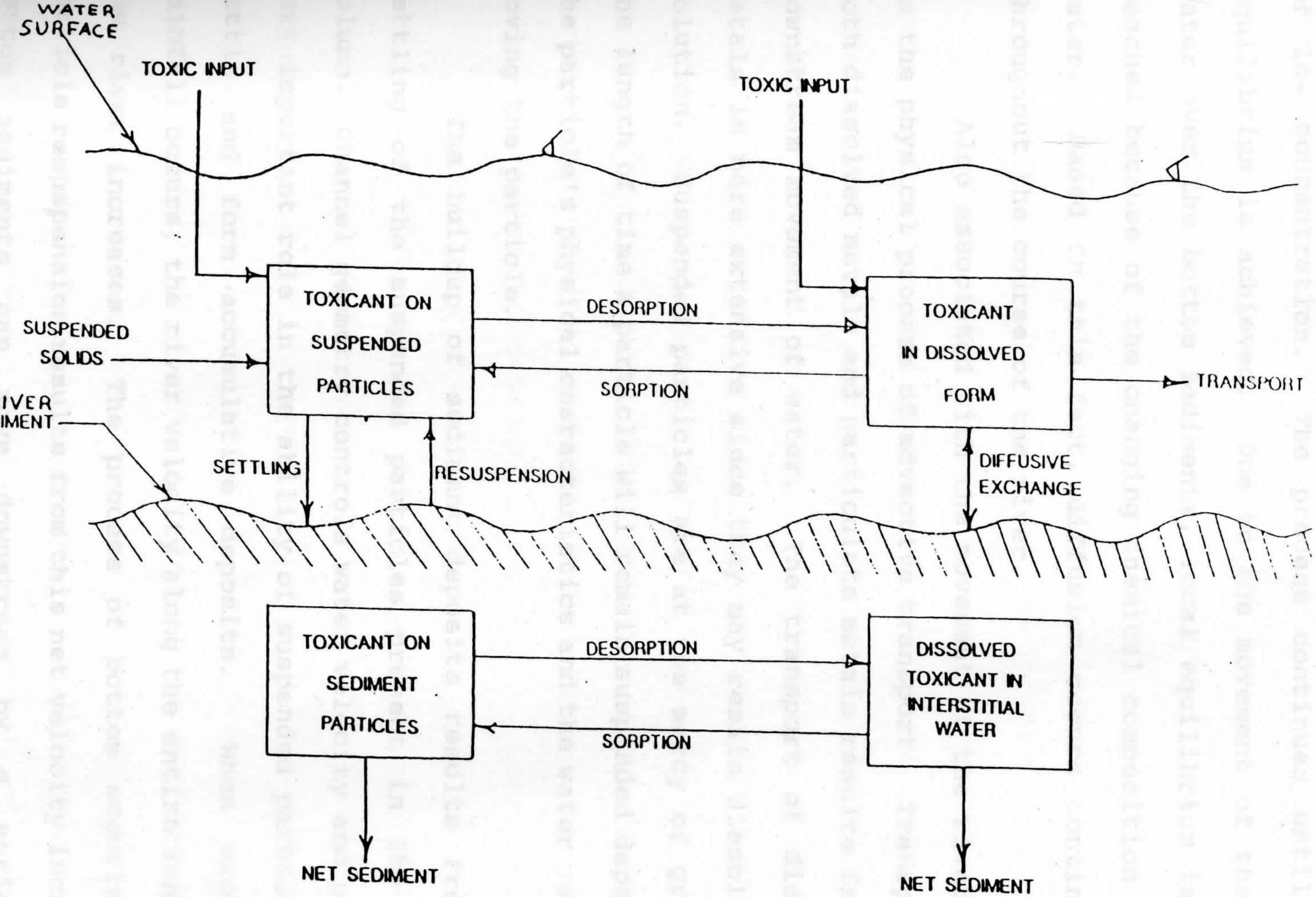


FIGURE 2.1: Schematic Representing the Various Physical and Chemical Processes Affecting Metal Distribution Within A River

the gradient to move from areas of high concentration to areas of low concentration. The process continues until local equilibrium is achieved. Due to the movement of the river water over the bottom sediments, local equilibrium is never reached because of the changing chemical composition of the water. Based on this fact, diffusion occurs continuously throughout the course of the river.

Also associated with the movement of the river water is the physical process of advective transport. Transport of both dissolved metals and particulate metals results from the downstream movement of water. The transport of dissolved metals is more extensive since they may remain dissolved in solution. Suspended particles are at the mercy of gravity. The length of time a particle will remain suspended depends on the particle's physical characteristics and the water velocity moving the particle.

The buildup of sediment deposits results from the settling of the suspended particles present in the water column. Channel geometry controls water velocity and plays a very important role in the ability of suspended particles to settle and form accumulative deposits. When excessive rainfall occurs, the river velocity along the entire length of the river increases. The process of bottom scouring and particle resuspension results from this net velocity increase. Bottom sediments can move downstream by a series of resuspension/deposition cycles, where the top layer of the bottom sediment is scoured away, and carried further downstream and deposited.

Review of Other Mahoning River Data

The Mahoning River has been studied throughout the years by various groups and organizations. Much of the water quality information collected is available through the STORET data base maintained by the USEPA. The STORET data which were collected before 1990 show elevated levels of metals in the water column (8). But, more recent data show that the level of various metals within the water column have been decreasing during the past ten years (8). Figure 2.3 and Figure 2.4 represent iron and copper concentrations, respectively, measured in the water column of the Mahoning River. The two figures suggest that the metal loadings to the river have decreased, resulting in lower concentrations of iron and copper in the water column.

The USEPA and Ohio EPA have periodically performed measurements of heavy metals in the Mahoning River bottom sediments. Table 2.3 shows metal levels recorded in 1975, 1980, and 1983. The metal concentrations for cadmium, chromium, copper, iron, lead, manganese, mercury, nickel and zinc were recorded for various sites and then classified based on the system of Kelly & Hite for classification of metal concentrations in river sediments (2). The classification of the sediments in Leavittsburg show that the metal

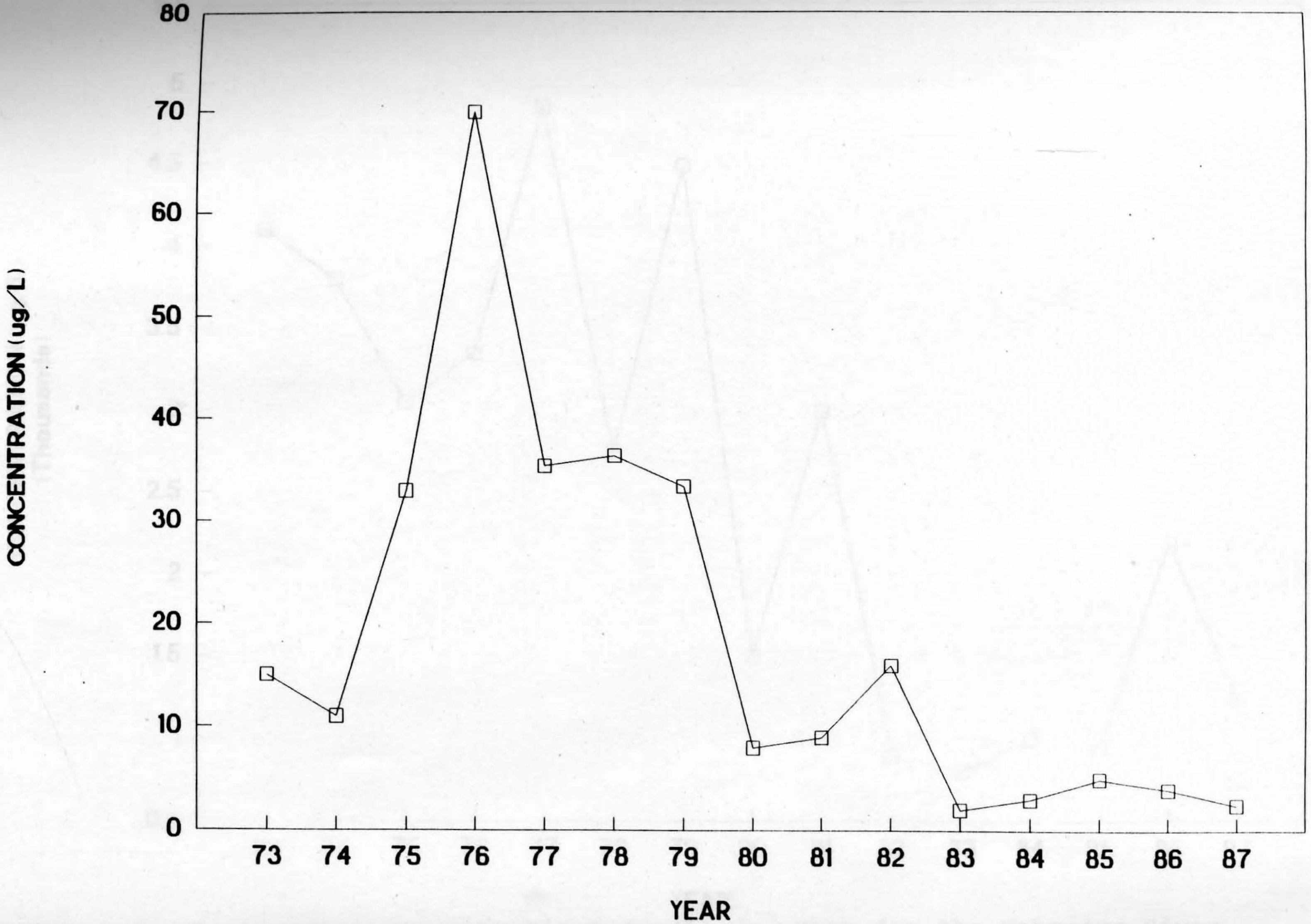


FIGURE 2.3: Iron (Fe) Concentrations (ug/L) vs. Year for the Mahoning River

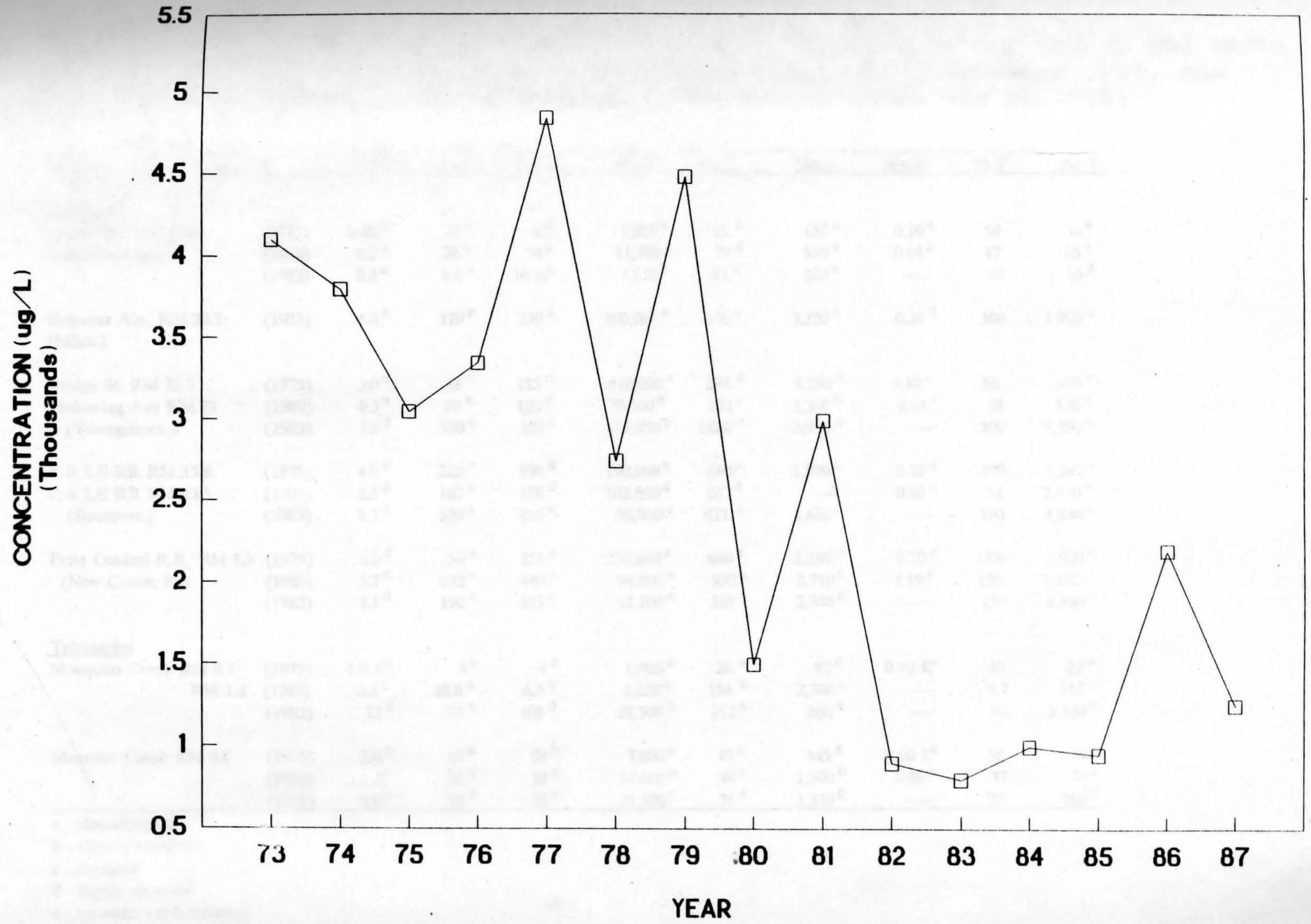


FIGURE 2.4: Copper (Cu) Concentrations (ug/L) vs. Year for the Mahoning River

TABLE 2.3: Chemical/Physical Results (mg/kg - dry weight) for Bottom Sediments from the Mahoning River During March 1975, December 1980, and November 1983 (Sampling Conducted by USEPA and OhioEPA)

Sampling Location (RM)		Cd-T	Cr-T	Cu-T	Fe-T	Pb-T	Mn-T	Mg-T	Ni-T	Zn-T
Mainstem										
Leavitt Rd RM 46.0	(1975)	1.0K[b]	15[a]	6[a]	7,800[a]	15.[a]	155[a]	0.10[a]	50	36[a]
(Leavittsburgh)	(1980)	0.2[a]	28[c]	14[a]	11,700[a]	79[d]	533[a]	0.04[a]	47	65[a]
	(1983)	0.2[a]	8.0[a]	10 K[a]	7,870[a]	47.[c]	280[a]	----	10	65[a]
Belmont Ave. RM 30.5 (Miles.)	(1983)	4.0[d]	370[e]	330[e]	200,000[e]	670[e]	3,220[d]	0.20[d]	360	1,990[e]
Bridge St. RM 22.7	(1975)	3.0[d]	28[c]	115[d]	410,000[e]	290.[e]	4,180[d]	0.10[a]	50	530[e]
Mahoning Ave RM 21	(1980)	0.3[a]	89[e]	130[d]	79,500[e]	232[e]	1,380[b]	0.14[c]	58	530[e]
(Youngstown.)	(1983)	7.0[d]	570[e]	350[e]	119,000[e]	1,060[e]	3,930[d]	----	300	7,390[e]
P & LE RR RM 15.8	(1975)	4.0[d]	220[e]	190[d]	190,000[e]	640[e]	1,970[c]	0.20[d]	190	1,240[e]
P & LE RR RM 13.5	(1980)	2.5[d]	167[e]	196[d]	103,500[e]	617[e]	----	0.80[e]	92	2,520[e]
(Struthers.)	(1983)	8.3[d]	520[e]	455[e]	56,900[e]	471.[e]	1,660[b]	----	190	4,830[e]
Penn Central R.R RM 1.5	(1975)	6.0[d]	150[e]	255[e]	230,000[e]	690[e]	2,150[c]	0.50[e]	200	2,900[e]
(New Castle, Pa)	(1980)	3.7[d]	672[e]	440[e]	94,800[e]	590[e]	2,710[c]	1.19[e]	138	3,020[e]
	(1983)	3.1[d]	190[e]	195[e]	67,100[e]	505[e]	2,940[d]	----	130	2,400[e]
Tributaries										
Mosquito Creek RM 0.4	(1975)	1.0 K[b]	3[a]	4[a]	1,400[a]	20.[a]	92[a]	0.10 K[a]	40	22[a]
RM 1.4	(1980)	0.5[b]	10.8[a]	6.5[a]	4,250[a]	154.[e]	2,360[c]	----	8.7	165[c]
	(1983)	12[d]	74[e]	105[d]	28,500[c]	112[e]	660[a]	----	60	3,100[e]
Meander Creek RM 0.8	(1975)	2.0[d]	18[b]	58[b]	7,800[a]	45[c]	345[a]	0.10 K[a]	50	134[c]
	(1980)	1.2 K[c]	22[b]	24[a]	67,000[e]	49[c]	1,300[b]	0.06[a]	37	78[a]
	(1983)	0.8[b]	50[d]	35[a]	29,100[c]	74[d]	1,370[b]	----	29	260[d]

a - non-elevated
b - slightly elevated
c - elevated
d - highly elevated
e - extreme contamination

concentrations are mostly non-elevated. Leavittsburg is located in a section of the Mahoning River that is upstream from all the industrial sources discharging to the river.

At the Belmont Avenue site, the metal concentrations begin to show the effects of the industrial sources that discharge to the river. With the exception of manganese, the metals analyzed show levels that are classified as being either elevated, highly elevated or extremely contaminated. Based on these limited data, the metal levels in the Mahoning River sediments have been, and still are classified as being at unsafe levels in the section of the river influenced by industry (15).

Classification Systems for Aquatic Sediments

There has not been a national or state classification system established to classify contaminant levels of heavy metals in river bottom sediments. Although a single classification system does not exist, several systems have been developed from various sediment studies conducted in the past. The systems which are available have been developed from specific data bases, and are aimed more at a specific aquatic system, rather than aquatic systems as a whole.

Two classification systems were chosen for this particular project, the Kelly & Hite (2) System, and the USEPA (16) System. The first system, the Kelly & Hite System, was based on sediment samples taken from various stream beds in the state of Illinois. The second system, the USEPA System, was based on sediment samples taken from 34 harbors in the Great Lakes region, during 1975 and 1976. Both of these systems were chosen because the sediments samples they were derived from were located in heavily industrialized regions. The classifications for the Kelly & Hite System, and the USEPA System are listed in Table 2.4 and 2.5, respectively.

James White, a Youngstown State University student, conducted a study in 1984 on several heavy metal concentrations in both the Mahoning River bottom sediments and Mahoning River water. Sediment measurements were performed by neutron activation analysis on samples from ten "pre-industrial" sites (i.e., above Warren and in tributaries) and thirteen "industrial" sites. Selected results of this study are summarized in Table 2.6.

TABLE 2.4: Kelly & Hite (2) Classification of Illinois Stream Sediments

CLASSIFICATION OF ILLINOIS STREAM SEDIMENTS

NUTRIENTS AND HEAVY METALS: Ranges of concentrations displayed and resultant groupings are based on one, two, four and eight standard deviations from background mean. Unless otherwise noted concentrations are in mg/kg sediment dry weight.

PARAMETER	NON-ELEVATED	SLIGHTLY ELEVATED	ELEVATED	HIGHLY ELEVATED	EXTREME
COD	< 90000	> 90000	> 132000	> 215000	> 380000
Total Kjeldahl Nitrogen	< 2300	> 2300	> 3200	> 5100	> 8800
Total Volatile Solids (%)	< 6.5	> 6.5	> 8.8	> 13	> 22
Total Phosphorus	< 80	> 80	> 1100	> 1700	> 3000
Arsenic	< 8.0	> 8.0	> 11	> 17	> 28
Chromium	< 16	> 16	> 23	> 38	> 60
Copper	< 38	> 38	> 60	> 100	> 200
Iron	< 18000	> 18000	> 23000	> 32000	> 50000
Manganese	< 1300	> 1300	> 1800	> 2800	> 6000
Mercury	< 0.07	> 0.07	> 0.01	> 0.17	> 0.30
Zinc	< 80	> 80	> 100	> 170	> 300

CADMIUM AND ORGANOCHLORIDE COMPOUNDS: Ranges of concentrations and resultant groupings are baesd on 50, 65, 80 and 95 percent distributions for all samples. Cadmium concentrations are in mg/kg and organochlorine concentrations are in mg/kg sediment dry weight.

PARAMETER	NON-ELEVATED	SLIGHTLY ELEVATED	ELEVATED	HIGHLY ELEVATED	EXTREME
Cadmium	< 0.5	> 0.5	> 0.1	> 2.0	> 20.0
Chlordane	< 5.0	> 5.0	> 6.0	> 10	> 40
Sum DOT	< 6.0	> 6.0	> 10	> 35	> 200
Diedrin	< 3.5	> 3.5	> 6.0	> 10	> 25
Heptachlor Epoxide	< 1.0	> 1.0	> 1.5	> 3.0	> 9.0
PCB'S	< 10	> 20	> 50	> 200	> 1500

TABLE 2.5: USEPA (16) Classification System for Sediment From Great Lakes Harbours

The following supplementary ranges used to classify sediments from Great Lakes harbours have been developed to the point where they are usable but are still sublect to modification by the addition of new data. These ranges are based on 260 samples from 34 harbours sampled during 1974 and 1975.

	Nonpolluted	Moderately Polluted	Heavily Polluted
Ammonia (mg/kg dry weight)	< 75	75 - 200	> 200
Cyanide " " "	< 0.10	0.10 - 0.25	> 0.25
Phosphours " " "	< 420	420 - 650	> 650
Iron " " "	< 17,000	17,000 - 25,000	> 25,000
Nickel " " "	< 20	20 - 50	> 50
Manganese " " "	< 300	300 - 500	> 500
Arsenic " " "	< 3	3 - 8	> 8
Cadmium " " "	*	*	> 6
Chromium " " "	< 25	25 - 75	> 75
Barium " " "	< 20	20 - 60	> 60
Copper " " "	< 25	25 - 50	> 50

* Lower limits not established

Table 2.6

Summary of Selected Results of Mahoning River Bottom Sediment Analyses by White (1984).

	Pre-industrialized Sites		Industrialized Sites	
Element	**Mean**	**Range**	**Mean**	**Range**
Chromium	105.0	43.0-290	371	80.4-584
Iron	34,500	18,300-79,400	141,000	66,700-270,000
Manganese	1,635	536-2,963	1,859	662-3,715
Zinc	344	82.0-1,350	1,850	327-3,330

CHAPTER III

METHODS AND PROCEDURES

Sampling Procedures

Core Locations

The locations chosen for core sampling were Newton Falls, Warren, Youngstown and Struthers, all in Ohio. The coring locations are shown on Figure 3.1. Newton Falls was chosen for coring because it represented a non-industrialized section of the river. Due to the quality of the water in Newton Falls, the city of Newton Falls uses the Mahoning as a drinking water source. The cores were taken in the general vicinity of the Newton Falls water treatment plant. The metals levels found in Newton Falls were assumed to represent the natural (background) levels of the various metals found in the river sediment. The Warren, Ohio sampling site was in the vicinity of Copperweld Steel Corporation (Copperweld) and the Luntz Corporation (Luntz), which are both located on North River Road in Warren. The Warren location was chosen due to the large number of steel mills, scrap yards, and metal fabrication-based industries located within the general vicinity. A few municipal wastewater dischargers are also located upstream of the Warren site (Newton Falls and Leavittsburg). It was felt that the metal concentrations found in this section of the river might produce the highest sediment metal levels due to the nature of the industry along

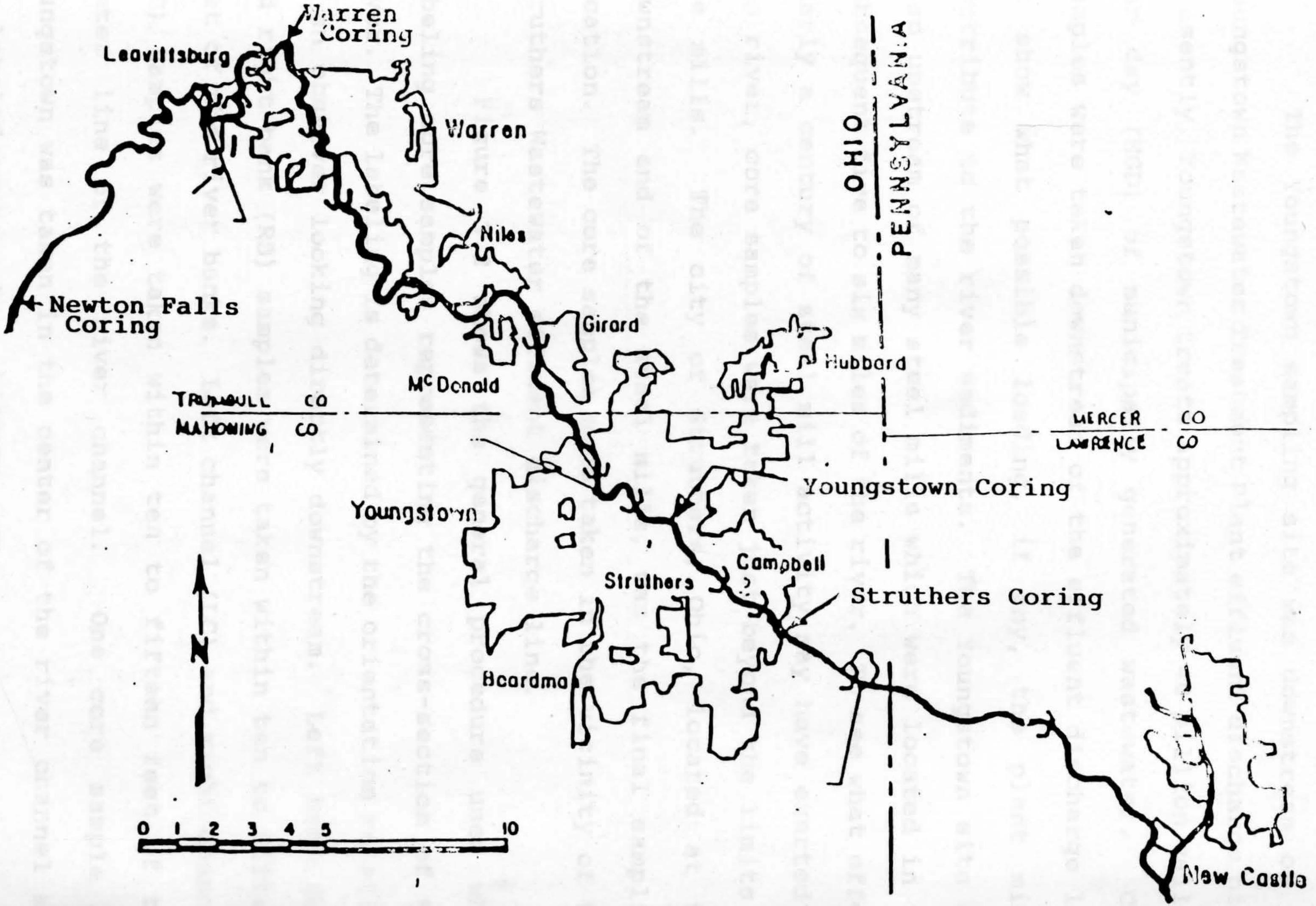


FIGURE 3.1: Coring Locations Along the Mahoning River

the banks of the river.

The Youngstown sampling site was downstream of the Youngstown Wastewater Treatment Plant effluent discharge pipe. Presently, Youngstown treats approximately 40 million gallons per day (MGD) of municipally generated wastewater. Core samples were taken downstream of the effluent discharge line to show what possible loading, if any, the plant might contribute to the river sediments. The Youngstown site was also upstream of many steel mills which were located in the subsequent five to six miles of the river. To see what effect nearly a century of steel mill activity may have exerted on the river, core samples were taken just beyond the limits of the mills. The city of Struthers, Ohio, located at the downstream end of the steel mills, was the final sampling location. The core samples were taken in the vicinity of the Struthers Wastewater effluent discharge line.

Figure 3.2 shows the general procedure used when labeling core samples representing the cross-section of the river. The labeling is determined by the orientation relative to an observer looking directly downstream. Left bank (LB) and right bank (RB) samples were taken within ten to fifteen feet of the river banks. Left channel (LC) and right channel (RC) samples were taken within ten to fifteen feet of the center line of the river channel. One core sample at Youngstown was taken in the center of the river channel and was labeled center channel (CCH). The center channel sample

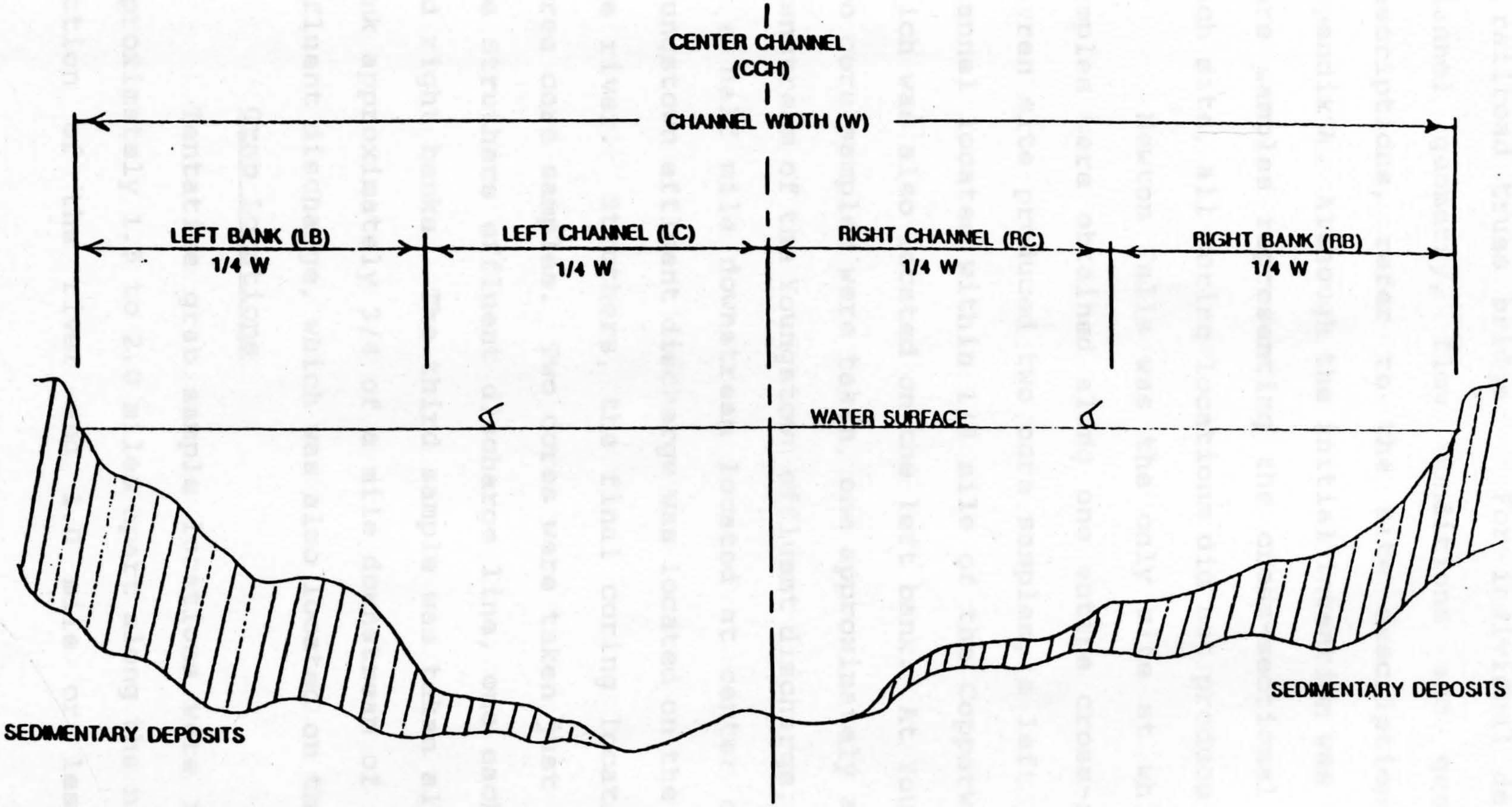


FIGURE 3.2: Schematic Drawing Showing the Cross-sectional Divisions Used For Core Sample Identification

was taken directly downstream from a center support column for a railroad truss bridge. For individual descriptions of channel geometry, flow conditions and general channel descriptions, refer to the site descriptions located in Appendix A. Although the initial intention was to obtain four core samples representing the cross-sectional variation at each site, all coring locations did not produce four cores.

Newton Falls was the only site at which four core samples were obtained along one entire cross-section. The Warren site produced two core samples, a left bank and left channel located within 1/8 mile of the Copperweld discharge which was also located on the left bank. At Youngstown, only two core samples were taken, one approximately a quarter mile downstream of the Youngstown effluent discharge, and the other at a half mile downstream located at center channel. The Youngstown effluent discharge was located on the right bank of the river. Struthers, the final coring location, produced three core samples. Two cores were taken just downstream of the Struthers effluent discharge line, one each on the left and right banks. The third sample was taken along the right bank approximately 3/4 of a mile downstream of the Struthers effluent discharge, which was also located on the right bank.

Grab Locations

Tentative grab sample locations were initially set approximately 1.5 to 2.0 miles apart along the non-industrial section of the river and 1.0 mile or less along the industrialized portion of the river. 37 sampling locations were chosen. During the sampling canoe trips, an additional 18 samples were taken in locations where general surroundings suggested a possible source of metals loading. A total of 61 grab samples were taken along the length of the river, 55 during two canoe trips and 6 additional samples taken during the coring trips. The following grab samples were taken during the core sampling trips, and are included on Figure 2.4: Warren: 9A and 9B; Youngstown: 28A and 28B; and Struthers: 34A and 34B. The locations of all grab samples are shown on Figure 3.3 and the distance the sample is located upstream of the river's mouth is listed in Table 3.1.

Equipment Description

Two separate sampling devices were used for the purpose of obtaining the grab samples and core samples. The core samples were obtained with a Wildco Corer which was modified by attaching four three-foot sections of threaded galvanized conduit pipe to allow driving of the core sampler into the river sediment. The samples were taken off a 14 foot flat-bottom aluminum row boat. Grab samples were taken with the use of a hard plastic 12 oz. mug attached to the end of a ten foot section of 2" x 2" wood. A beveled end on the grab sampler provided a means of probing the river bottom to estimate river depth and locate sediment deposits suitable for sampling..

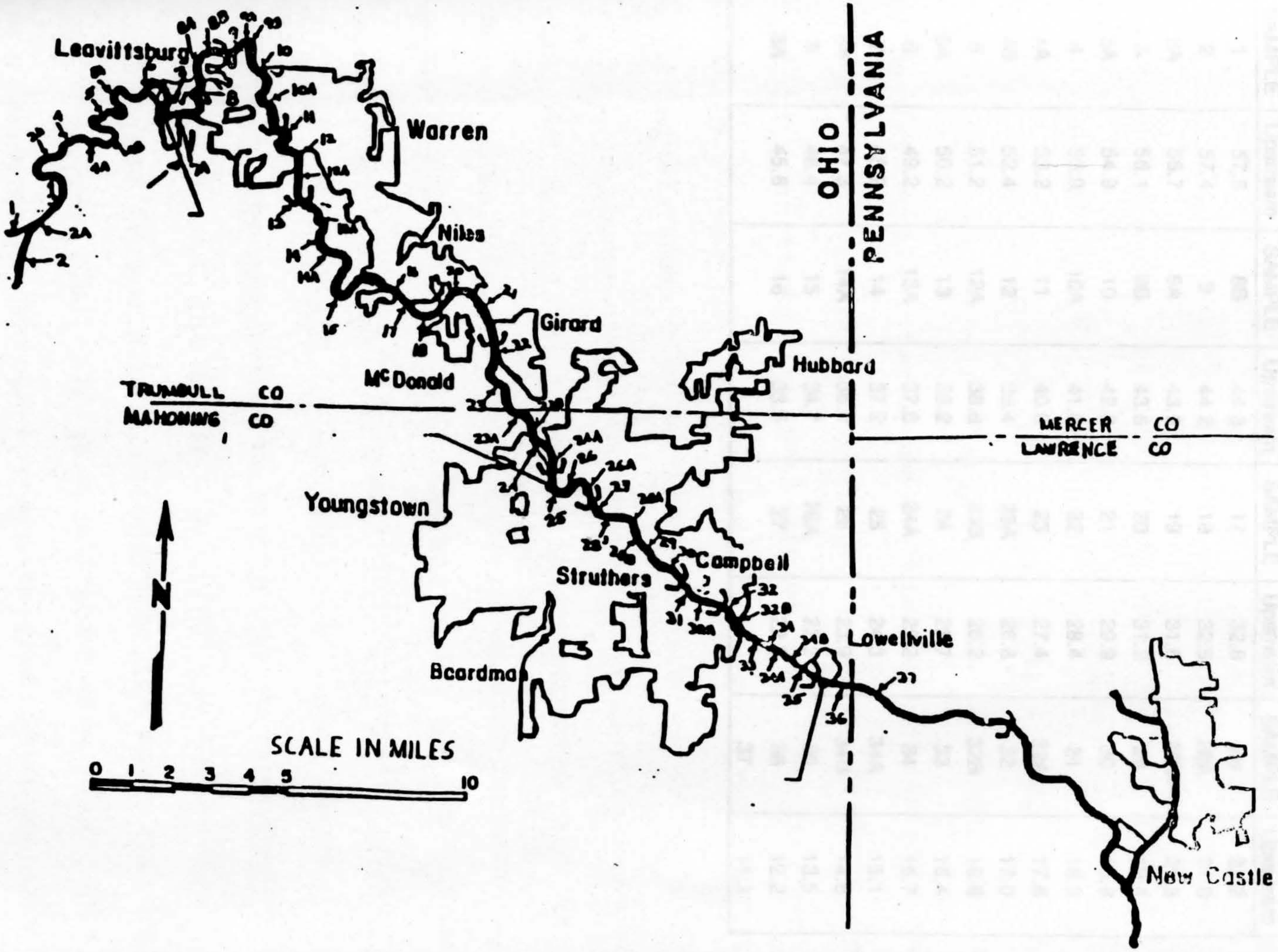


FIGURE 3.3: Location Of Grab Samples Taken Along The Mahoning River

TABLE 3.1: Location of Grab Samples in Miles Upstream of Mouth of River (miles)

GRAB SAMPLE	Miles Upstream	GRAB SAMPLE	Miles Upstream	GRAB SAMPLE	Miles Upstream	GRAB SAMPLE	Miles Upstream
1	57.5	8B	44.8	17	32.8	28	22.2
2	57.4	9	44.2	18	32.5	28A	21.8
2A	56.7	9A	43.9	19	31.6	28B	21.3
3	56.1	9B	43.6	20	31.2	29	19.4
3A	54.9	10	42.8	21	29.9	30	18.9
4	53.9	10A	41.8	22	28.4	31	18.2
4A	53.2	11	40.6	23	27.4	32A	17.6
4B	52.4	12	39.4	23A	26.8	32	17.0
5	51.2	12A	38.8	23B	26.2	32B	16.6
5A	50.2	13	38.2	24	25.7	33	16.4
6	49.2	13A	37.8	24A	25.2	34	15.7
7	48.2	14	37.2	25	24.3	34A	15.1
7A	47.3	14A	36.0	26	23.9	34B	14.6
8	46.4	15	34.7	26A	23.2	35	13.5
8A	45.6	16	33.5	27	22.8	36	12.2
						37	11.1

Analytical Procedures

Sample Preparation

CORE SAMPLES: The core samples extracted from the river were capped on both ends upon removal from the coring sampler. Then the plastic coring tubes were properly labeled with a grease pencil to facilitate identification in future handling. Once in the lab, the samples were placed in a vertical position and the excess tube extending above the water level within the tube was removed. Each tube was then placed in a freezer compartment in as close to a vertical position as possible. The samples were then stored for at least 24 hours at 0 °C, allowing the samples to solidify, thus enabling the sample to be sectioned.

Once the cores had frozen, they were removed one at a time and marked in one-inch increments for the first six inches and two-inch increments from six inches on. Each segment was cut using a hardened steel hacksaw blade. The blade was thoroughly rinsed with deionized water between samples and wiped clean with a paper towel. Metal contamination was believed not to result from cutting due to the hardness of the blade. A plastic dish was then labeled with a red grease pencil, specifying the core and depth from which it was cut. All of the dishes were then placed in an incubator at 40 °C for approximately 48 hours or until visual inspection suggested that the samples were thoroughly air-dried.

After drying, each sample was removed and then pulverized with a mortar and pestle (which had been acid washed and rinsed with deionized water). The sediment was worked until a fine powder remained or the smallest particle size was obtained. The powder produced was then placed in a 150 ml plastic tri-pour beaker (which had been previously acid washed and rinsed with deionized water). Each sample was then labeled. Parafilm was placed over the mouth of the beaker and the sample was placed in a desiccator to maintain a minimal moisture content. Once all of the core samples had been processed in the same manner and placed in the desiccator, the moisture content of each sample was determined.

Moisture content was obtained by numbering and placing aluminum tins in a Blue M oven and drying for one hour at 103 °C. The tins were then removed and placed in a desiccator and allowed to cool to room temperature. Once cooled, the tins were individually removed, and weighed on a electronic balance. Then, a small amount of sediment was placed in the tin and the total weight recorded. All of the sediment samples were again placed in the oven for 24 hours at 103 °C to allow moisture to evaporate. The samples were again placed in the desiccator and allowed to dry to room temperature before the tins and sediment were weighed again. Using the three weight measurements for each tin (dry tin, tin + air-dried sediment and tin + oven-dried sediment), the moisture content of each sample was determined using the following equation:

$$moisturecontent(\%) = \frac{tin+wetsed.(g) - tin+drysed(g)}{tin+wetsed(g) - drytin(g)} * 100$$

Moisture contents registering above 1.0 % were recorded to adjust the final sediment metals concentrations for water content.

GRAB SAMPLES: Grab samples were obtained by using a 12 ounce hard plastic mug attached to a ten-foot section of 2"x 2" wooden pole. The grab sampler was used to probe the river bottom to determine where possible sediment deposits existed. The plastic mug was then carefully lowered to the river bottom and dragged through the sediment to obtain a sample representive of the location sampled.

Once a sufficient amount of sediment was obtained, the sample was carefully removed with a clean plastic spoon and placed in a 250 ml plastic sample bottle which had been previously washed with 10% nitric acid and rinsed with deionized water. Each sample bottle was marked with a number in grease pencil to provide proper identification of the sample for the designated site. The grab sampler was then thoroughly rinsed with river water to eliminate possible cross-contamination with the next sample taken. At the lab facilities, the samples were preserved by refrigeration at 4 °C until they were ready for further preparation. The grab samples were processed in the same manner as the core samples;

however, the grab samples did not require freezing or cutting prior to drying.

Metal Analysis Procedures

DIGESTION: In preparation for the digestion of samples in a CEM Corp. MSD-81D microwave digestion system, the teflon digestion vessels, lids and pressure discs were acid washed and thoroughly rinsed with deionized water. The digestion vessels were numbered in sequential order to allow proper identification of the samples following digestion. Samples that had been dried, crushed and placed in a desiccator were ready for digestion. A Mettler Model AE100 electronic balance was used to measure out as close to one gram of sediment as possible. Carefully, the one gram of sediment was poured into a digestion vessel and 10 mL of double distilled Nitric Acid was added. The cap and pressure lid were then carefully placed on the digestion vessel and tightened to a torque of 110 ft-lb at the capping station. Each pressure ring was designed to prevent the pressure within the digestion vessel from exceeding 120 pounds per square inch (psi).

A maximum of six vessels were placed in the digester at one time to prevent overheating and venting of the samples. Each sample was individually placed in the vessel holder and a vent tube was connected to the top of each vessel to vent any gas into a condensing reservoir. The samples were digested at 90% power for the first two minutes and thirty seconds and then 65% power for an additional 55 minutes.

Following digestion, the samples were allowed to cool to room temperature and the caps were removed from the digestion vessels with the aid of the capping station. The caps and pressure disks of each vessel were rinsed with deionized water washing the remaining sample into its respective vessel. Once all of the lids had been properly removed and rinsed, 5 mL of 30% hydrogen peroxide was added to each sample in 1 mL increments to prevent the samples from foaming over. High concentrations of petroleum products were believed to be responsible for the foaming. The samples were allowed to stabilize before moving them, thus preventing agitation that could produce foaming and cause a chemical burn.

Addition of the hydrogen peroxide caused the sample temperatures to rise, thus requiring that gloves be worn during sample handling procedures. The samples were then carefully poured into a 100 mL volumetric flask, being careful to prevent any solid particles from entering the sample. Once all the sample had been poured into the volumetric flask, additional deionized water was added to bring the total volume up to 100 mL. The samples were then transferred to 125 mL plastic sample bottles and refrigerated. The digestion process was identical for both the grab and core samples.

ANALYSIS: Prior to analysis of the samples with the Atomic Absorption Spectrophotometer (AA), standards of known concentrations were prepared for each element to be analyzed. The standards were made by diluting a 1000 ppm solution of the desired element with deionized water to achieve the desired range of concentrations and acidifying with concentrated nitric acid. Most of the standards were made up in 100 mL volumes, but the standard used to maximize the absorbance readings on the AA were made up in 250 mL quantities.

Prior to flame analysis, the Perkin-Elmer Model 2380 Atomic Adsorption (AA) Spectrophotometer was properly set-up, as specified by the operation manual (7). The specified wavelength, air/acetylene fuel mixture, burner head position, lamp energy reading and flame absorbance were all optimized prior to analyzing samples. A blank was aspirated periodically along with samples of known concentrations, to assure the absorbance of the AA did not drift during analysis. For each sample, fifteen readings of a half second duration were taken and the average concentration was recorded. The slit openings and wavelength settings used for the various elements are summarized in Table 3.2.

TABLE 3.2

Slit Openings and Wavelength Settings for Constituents Analyzed (7)

ELEMENT	SLIT OPENING (nM)	WAVELENGTH (nM)
Cadmium	0.7	232.2
Chromium	0.7	357.9
Copper	0.7	324.8
Iron	0.2	305.9
Lead	0.7	217.0
Manganese	0.2	280.1
Nickel	0.2	232.2
Zinc	0.7	213.9

CHAPTER IV

RESULTS & DISCUSSION

Grab Samples

All heavy metal results on grab samples are presented in Table 4.1. The results for each individual metal are discussed below.

Cadmium

The concentrations of cadmium (Figure 4.1) were below the detection limit (1.5 mg/kg) along most of the river, with elevated concentrations occurring at only two separate locations. The two spikes in the cadmium levels were 5.3 mg/kg and 2.3 mg/kg recorded at sample locations 9B and 28A, respectively. Sample 9B was taken during the core sample trip at the Warren coring location directly downstream from Copperweld Steel's industrial treatment plant discharge. Sample 28A was taken 300 to 500 feet downstream from Youngstown's municipal wastewater treatment plant discharge. The Youngstown sample was also taken during the core sampling trip at the Youngstown coring location.

A possible explanation for the elevated cadmium levels may be the presence of the industrial discharge sources which begin to appear on the banks of the Mahoning River in Warren, Ohio. Sample 9B was located directly downstream from an industrial discharge source which may pose a major impact on

TABLE 4.1: Grab sample concentrations (mg/kg) vs distance upstream of river mouth (miles)

SAMPLE NAME	DISTANCE UPSTREAM OF MOUTH	Manganese Mn (280.1)	Copper Cu (324.8)	Zinc Zn (213.9)	Cadmium Cd (232.2)	Nickel Ni (232.2)	Lead Pb (217.0)	Chromium Cr (357.9)	Iron Fe (305.9)
37	11.1	1957	199	1025	0	69	362	43	46210
36	12.2	1696	212	1265	0	66	490	45	41840
35	13.5	1623	236	1725	0	95	690	129	29850
34B	14.6	1968	2357	277	0	78.2	129	91.6	55850
34A	15.1	1517	2700	1099	0	44.9	285	154.1	34600
34	15.7	2106	145	345	0	57	205	45	72200
33	16.4	1660	113	700	0	52	266	42	33510
32B	16.6	1466	59	310	0	38	133	34	21820
32A	17	1447	110	580	0	51	223	45	41020
32	17.6	2006	283	1825	0	149	679	50	42980
31	18.3	1236	71	465	0	35	162	36	25830
30	18.9	1381	98	580	0	46	184	50	28500
29	19.4	2074	117	730	0	52	284	47	63650
28B	21.3	1511	1864	678	2.3	87.6	286	115.3	36520
28A	21.75	1458	1865	285.7	0	58	235	76.1	34590
28	22.2	633	197	1345	0	81	680	119	15970
27	22.8	1538	98	545	0	55	257	50	36600
26A	23.2	1416	144	840	0	86	324	80	21920
26	23.9	1517	134	880	0	63	240	74	28650
25	24.3	2836	154	595	0	15	440	21	55150
24A	25.2	1420	37	1555	0	21	483	42	56310
24	25.7	1889	443	1015	0	192	425	183	46540
23B	26.2	1649	215	1435	0	167	312	322	20650
23A	26.75	1265	186	1160	0	136	234	260	25610
23	27.4	805	77	510	0	48	144	51	19790
22	28.4	1231	103	685	0	58	138	51	37290
21	29.9	1437	168	1295	0	140	325	145	11300
20	31.2	2162	485	1110	0	130	382	65	30920
19	31.6	1372	156	895	0	113	210	126	14580
18	32.5	1229	126	760	0	109	179	101	13240
17	32.8	960	107	850	0	76	216	101	8600
16	33.5	2151	546	1825	0	388	456	231	31290
15	34.7	794	510	1375	0	174	437	74	32650
14A	36	1530	88	290	0	65	90	43	16910
14	37.2	2071	155	705	0	115	190	81	18350
13A	37.8	2707	291	2310	0	270	1151	174	29840
13	38.2	1497	1238	1055	0	319	285	92	30050
12A	38.8	2121	779	945	0	386	243	193	48670
12	39.4	1522	950	2020	0	381	426	133	12170
11	40.6	1725	125	352	0	220	101	140	11620
10A	41.8	2668	124	233	0	273	154	263	12940
10	42.8	2446	233	91	0	439	127	429	28880
9B	43.2	3470	485	170	5.3	1014	618	910	237000
9A	43.8	750	42	67	1.2	94	52	139	38000
9	44.2	600	13	62	0	43	20	24	13220
8B	44.8	794	12	45	0	35	22	23	10320
8A	45.6	592	23	84	0	51	28	27	15500
8	46.4	681	17	73	0	47	30	29	19010
7A	47.3	541	20	82	0	32	30	22	16730
7	48.2	475	17	83	0	45	32	24	15860
6	49.2	425	16	70	0	33	26	21	14420
5A	50.2	1360	36	189	0	54	43	35	26510
5	51.25	1002	29	145	0	54	48	36	27820
4B	52.4	610	16	74	0	34	27	22	15020
4A	53.2	567	21	99	0	44	36	28	19400
4	53.9	585	19	73	0	46	30	31	15530
3A	54.9	697	15	63	0	34	29	27	13890
3	56.1	2344	18	72	0	48	31	24	15830
2A	56.7	778	13	73	0	32	29	21	11240
2	57.4	409	16	64	0	31	28	19	12690
1	57.5	298	6	21	0	4	13	11	6210

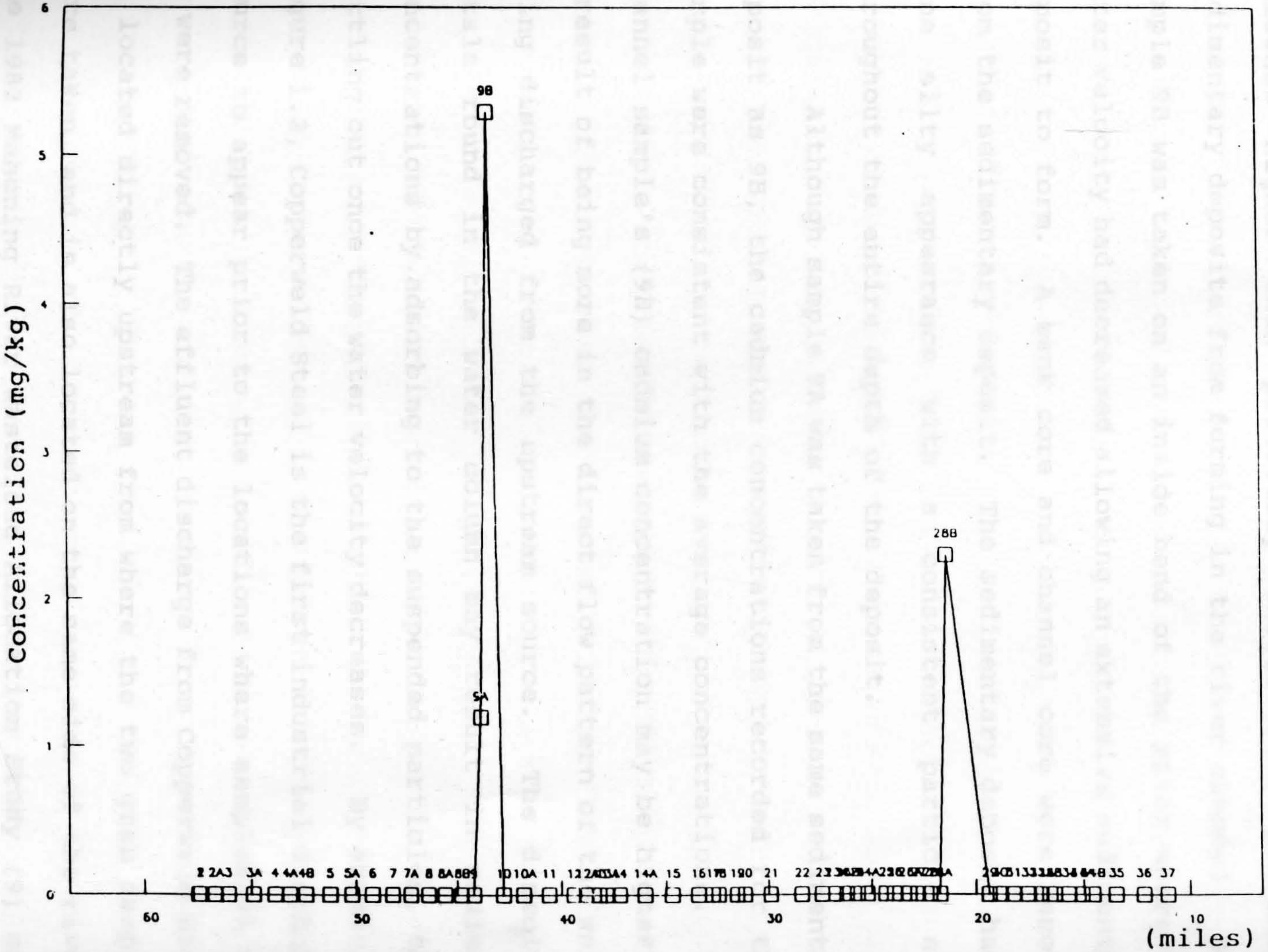


FIGURE 4.1: Cadmium (Cd) Concentrations (mg/kg) vs. Location Upstream of River Mouth (miles)

the metal levels encountered in this section of the river. In the Warren section of the river, the water velocity was somewhat higher than previously encountered, preventing sedimentary deposits from forming in the river channel. But, sample 9B was taken on an inside bend of the river where the water velocity had decreased allowing an extensive sedimentary deposit to form. A bank core and channel core were removed from the sedimentary deposit. The sedimentary deposit had a fine silty appearance with a consistent particle size throughout the entire depth of the deposit.

Although sample 9A was taken from the same sedimentary deposit as 9B, the cadmium concentrations recorded for this sample were consistent with the average concentrations. The channel sample's (9B) cadmium concentration may be higher as a result of being more in the direct flow pattern of the waste being discharged from the upstream source. The dissolved metals found in the water column may result in sediment concentrations by adsorbing to the suspended particles, then settling out once the water velocity decreases. By examining Figure 1.2, Copperweld Steel is the first industrial discharge source to appear prior to the locations where samples 9A and 9B were removed. The effluent discharge from Copperweld Steel is located directly upstream from where the two grab samples were taken, and is also located on the same side of the river. The 1983 Mahoning River Wasteload Allocation Study (9) says that "Copperweld currently discharges negligible loads of chromium, lead, nickel, and zinc." Thus Copperweld is not a definite source of all metals loading to the Mahoning River. Although Copperweld Steel's discharge may not present the only source of metals loading to the river in this portion, it is believed that Copperweld is a major contributor to the higher sediment cadmium level associated with this section of the river.

Sample 28A, which was taken at the Youngstown coring location, recorded the second highest cadmium concentration, 2.3 mg/kg. Youngstown's municipal wastewater treatment plant discharge culvert is located directly upstream from where sample 28A was removed. Higher cadmium levels may be generated through the various industrial sources and municipal sources which the plant treats prior to discharge to the river. Since cadmium is on the Priority Toxic Water Pollutants list, industrial and municipal dischargers that discharge directly to a receiving surface water are required to control the cadmium loading rates. The rates which the dischargers must maintain are set by the Ohio Environmental Protection Agency (EPA) and are based on the present levels within the receiving water and what impact the source would have on the receiving water.

Chromium

Figure 4.2 indicates that sediment chromium concentrations between Newton Falls and Warren averaged about 30.0 mg/kg. This level for chromium is assumed to be the

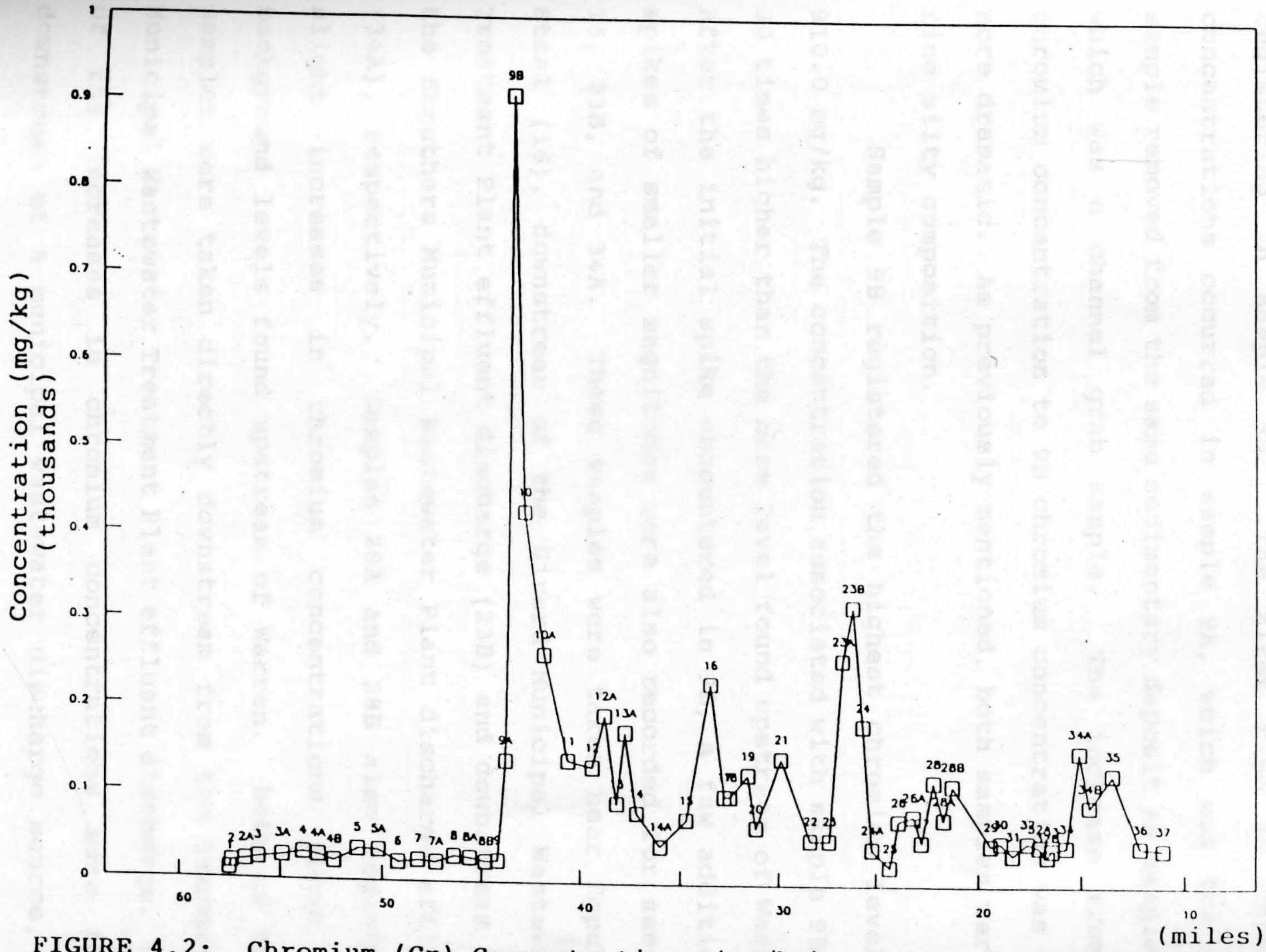


FIGURE 4.2: Chromium (Cr) Concentrations (mg/kg) vs. Location Upstream of River Mouth (miles)

background or natural level occurring within the river. Once again, as with the cadmium concentrations, an initial spike in the chromium concentration occurred in Warren, Ohio, registering in sample 9B. The first rise in chromium concentrations occurred in sample 9A, which was the bank sample removed from the same sedimentary deposit as sample 9B, which was a channel grab sample. The increase from 9A chromium concentration to 9B chromium concentration was much more dramatic. As previously mentioned, both samples were of fine silty composition.

Sample 9B registered the highest chromium level of 910.0 mg/kg. The concentration associated with sample 9B was 30 times higher than the base level found upstream of Warren. After the initial spike encountered in 9B, a few additional spikes of smaller magnitudes were also recorded for samples 16, 23B, and 34A. These samples were taken near Republic Steel (16), downstream of the Girard Municipal Wastewater Treatment Plant effluent discharge (23B) and downstream from the Struthers Municipal Wastewater Plant discharge effluent (34A), respectively. Samples 28A and 28B also registered slight increases in chromium concentrations above the background levels found upstream of Warren. Both of these samples were taken directly downstream from the Youngstown Municipal Wastewater Treatment Plant effluent discharge. Most of the increases in chromium concentrations were found downstream of a municipal wastewater discharge source, and suggest that the effluent from these dischargers may be sources of chromium loadings to the river.

Following the initial spike recorded for sample 9B, chromium levels showed a tendency to decrease back down to the background levels. The number of sources which discharge to the river are not as concentrated in the lower portion of the river approaching the Pennsylvania line as they are in the stretch between Youngstown and Warren. Chromium is regulated in the Primary Drinking Water Standards and also listed on the Priority Toxic Water Pollutant list (6,13,17).

Copper

Figure 4.3 shows the variations in copper concentrations recorded in the length of the Mahoning River encompassed in this study. For copper, the background levels upstream of Warren were consistently below 40 mg/kg. The first initial rise in copper concentrations occurred in sample 9B, and then additional elevated levels occurred in samples 12, 13, 15, 20, 28A and 34A. The highest concentration was registered in sample 34A (3700 mg/kg), which was taken downstream from the Struthers Municipal Wastewater Treatment Plant effluent discharge culvert. All the samples which registered high copper concentrations were located downstream from steel production mills which discharged into the river. The following mills coincide with the previously mentioned samples: Copperweld Steel (9B), Wheeling Pittsburgh Steel

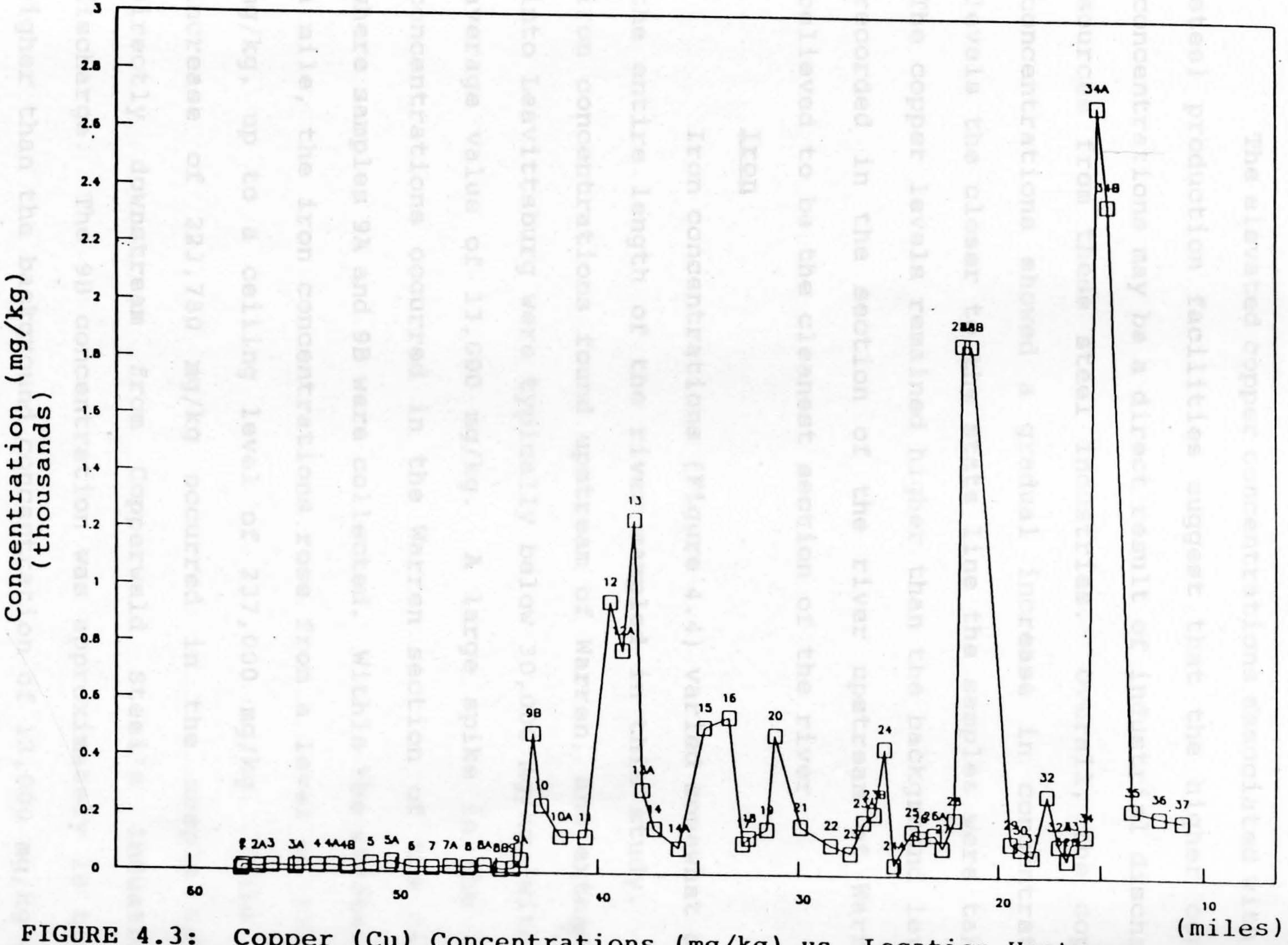


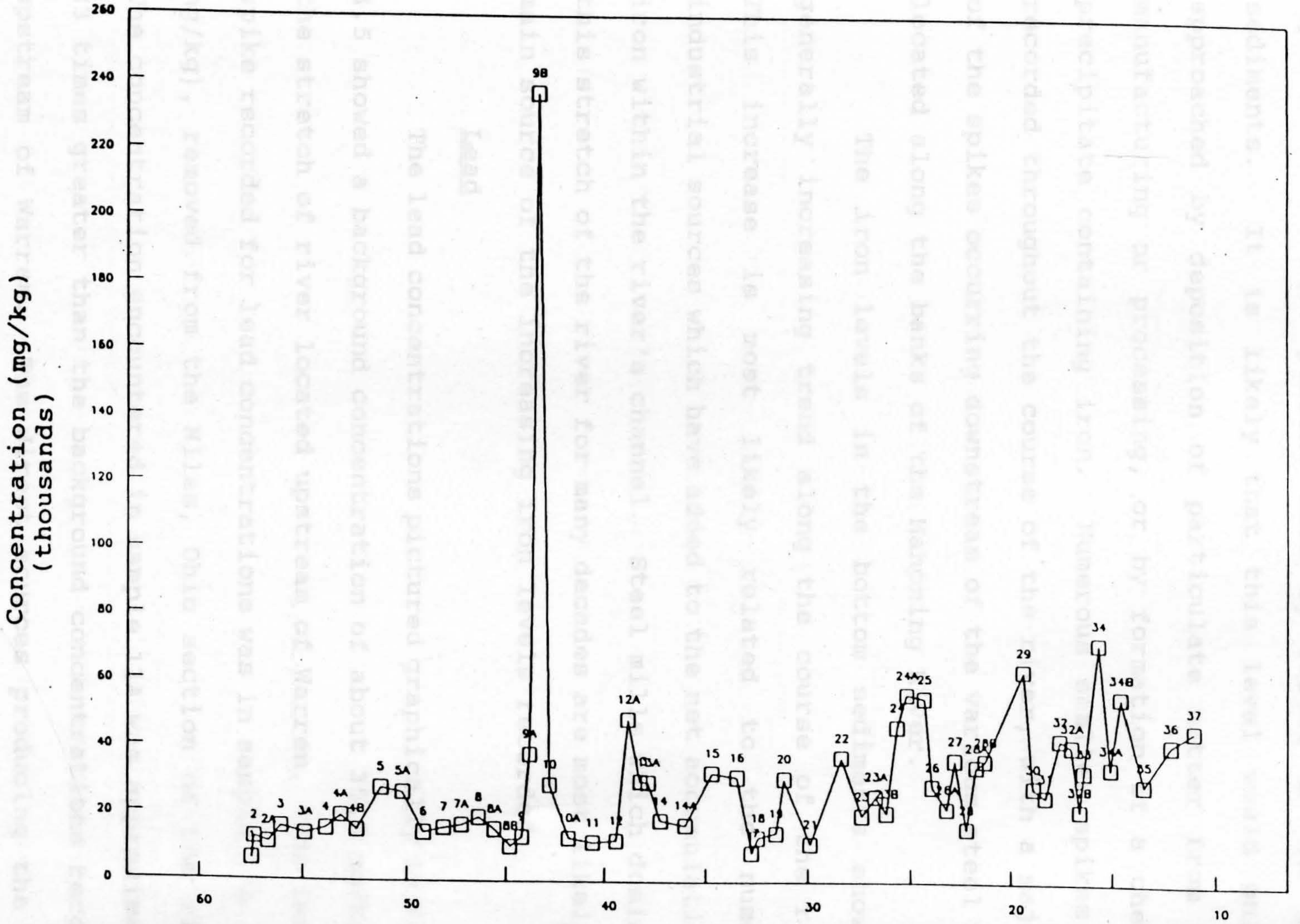
FIGURE 4.3: Copper (Cu) Concentrations (mg/kg) vs. Location Upstream of River Mouth (miles)

(12), Republic Steel, Warren (13), Republic Steel, Niles (15), United States Steel, McDonald (20), United States Steel, Youngstown (28A) and Republic Steel Corp, Youngstown (34A).

The elevated copper concentrations associated with the steel production facilities suggest that the higher copper concentrations may be a direct result of industrial discharge sources from these steel industries. Overall, the copper concentrations showed a gradual increase in concentration levels the closer to the state line the samples were taken. The copper levels remained higher than the background levels recorded in the section of the river upstream of Warren, believed to be the cleanest section of the river.

Iron

Iron concentrations (Figure 4.4) varied somewhat over the entire length of the river sampled in this study. The iron concentrations found upstream of Warren, and extending into Leavittsburg were typically below 30,000 mg/kg, with an average value of 13,000 mg/kg. A large spike in the iron concentrations occurred in the Warren section of the river where samples 9A and 9B were collected. Within the stretch of a mile, the iron concentrations rose from a level of 13,220 mg/kg, up to a ceiling level of 237,000 mg/kg. This net increase of 223,780 mg/kg occurred in the sample taken directly downstream from Copperweld Steel's industrial discharge. The 9B concentration was approximately 18 times higher than the background concentration of 13,000 mg/kg and



FICURE 4.4: Iron (Fe) Concentrations (mg/kg) vs. Location Upstrem of River Mouth (miles)

3.3 times higher than second highest peak concentration encountered. The concentration measured in sample 9B is equivalent to 23.7 percent iron by weight in the bottom sediments. It is likely that this level would only be approached by deposition of particulate matter from steel manufacturing or processing, or by formation of a chemical precipitate containing iron. Numerous smaller spikes were recorded throughout the course of the river, with a majority of the spikes occurring downstream of the various steel mills located along the banks of the Mahoning River.

The iron levels in the bottom sediments showed a generally increasing trend along the course of the river. This increase is most likely related to the numerous industrial sources which have added to the net accumulation of iron within the river's channel. Steel mills which dominated this stretch of the river for many decades are most likely the main source of the increasing iron levels recorded.

Lead

The lead concentrations pictured graphically in Figure 4.5 showed a background concentration of about 35.0 mg/kg for the stretch of river located upstream of Warren. The largest spike recorded for lead concentrations was in sample 13A (1151 mg/kg), removed from the Niles, Ohio section of the river. The concentration encountered in sample 13A was approximately 33 times greater than the background concentrations recorded upstream of Warren. The direct sources producing the high

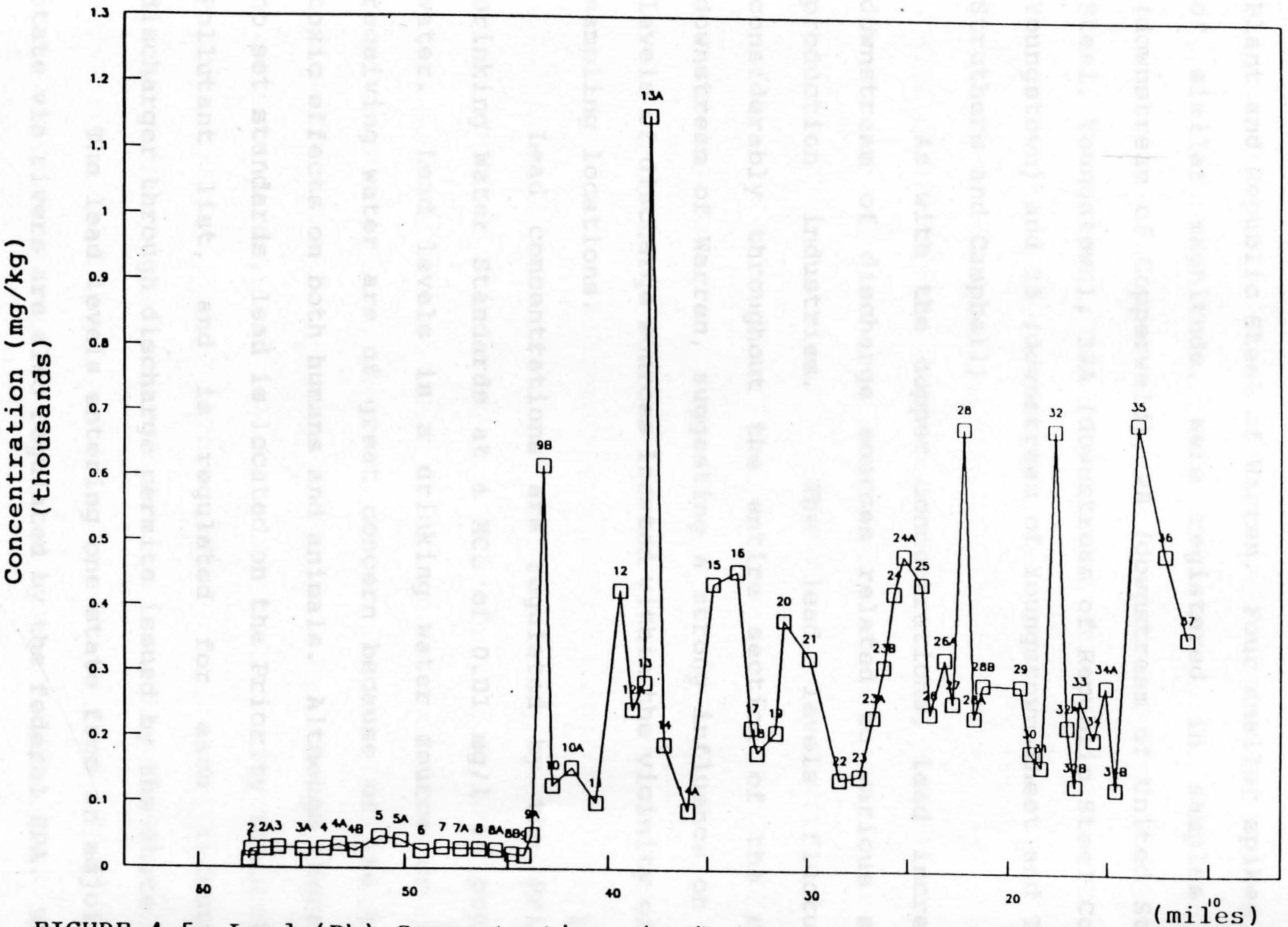


FIGURE 4.5: Lead (Pb) Concentrations (mg/kg) vs. Location Upstream of River Mouth (miles)

level found in sample 13A could not be pin-pointed, but the two point sources in the immediate upstream vicinity of the sample location were the Warren Municipal Wastewater Treatment Plant and Republic Steel of Warren. Four smaller spikes, all of similar magnitude, were registered in samples 9B (downstream of Copperweld), 28 (downstream of United States Steel, Youngstown), 32A (downstream of Republic Steel Corp., Youngstown) and 35 (downstream of Youngstown Sheet and Tube, Struthers and Campbell).

As with the copper concentrations, lead increased downstream of discharge sources related to various steel production industries. The lead levels fluctuated considerably throughout the entire section of the river downstream of Warren, suggesting a strong influence on lead levels of discharge sources located within the vicinity of the sampling locations.

Lead concentrations are regulated by the Primary Drinking Water Standards at a MCL of 0.01 mg/l in potable water. Lead levels in a drinking water source or in a receiving water are of great concern because of its known toxic effects on both humans and animals. Although there are no set standards, lead is located on the Priority Toxic Water Pollutant list, and is regulated for each industrial discharger through discharge permits issued by the state EPA.

The lead levels entering one state from an adjoining state via rivers are also regulated by the federal EPA. Where the Mahoning River crosses the Ohio/Pennsylvania border, the lead levels are tested and checked to see if they are below the limits set by the Federal EPA. Ohio frequently exceeds the allowable level of lead in the Mahoning River as it passes into Pennsylvania. The sediment lead concentrations gradually increased as the river approached the Ohio/Pennsylvania state line. Industrial discharge sources are also believed to be the main contributors to the increasing levels of lead found in the Mahoning River bottom sediment. There are also a number of municipal wastewater treatment plants located along the lower section of the Mahoning River which are also believed to play a contributing role in lead loadings to the river.

Manganese

Manganese concentrations versus river mile are shown on Figure 4.6. Sediment manganese concentrations varied extensively over the entire course of the Mahoning River sampled during this study. A background concentration was difficult to determine since the manganese concentrations show numerous variations even upstream of Warren. This suggests that soil composition of the area in the vicinity of the river may have an impact on the bottom sediment manganese concentrations found within the river. The highest concentration of manganese recorded in the river was found in sample 9B (3470 mg/kg), and was approximately 1.2 times higher than the second highest concentration found in sample 25. The

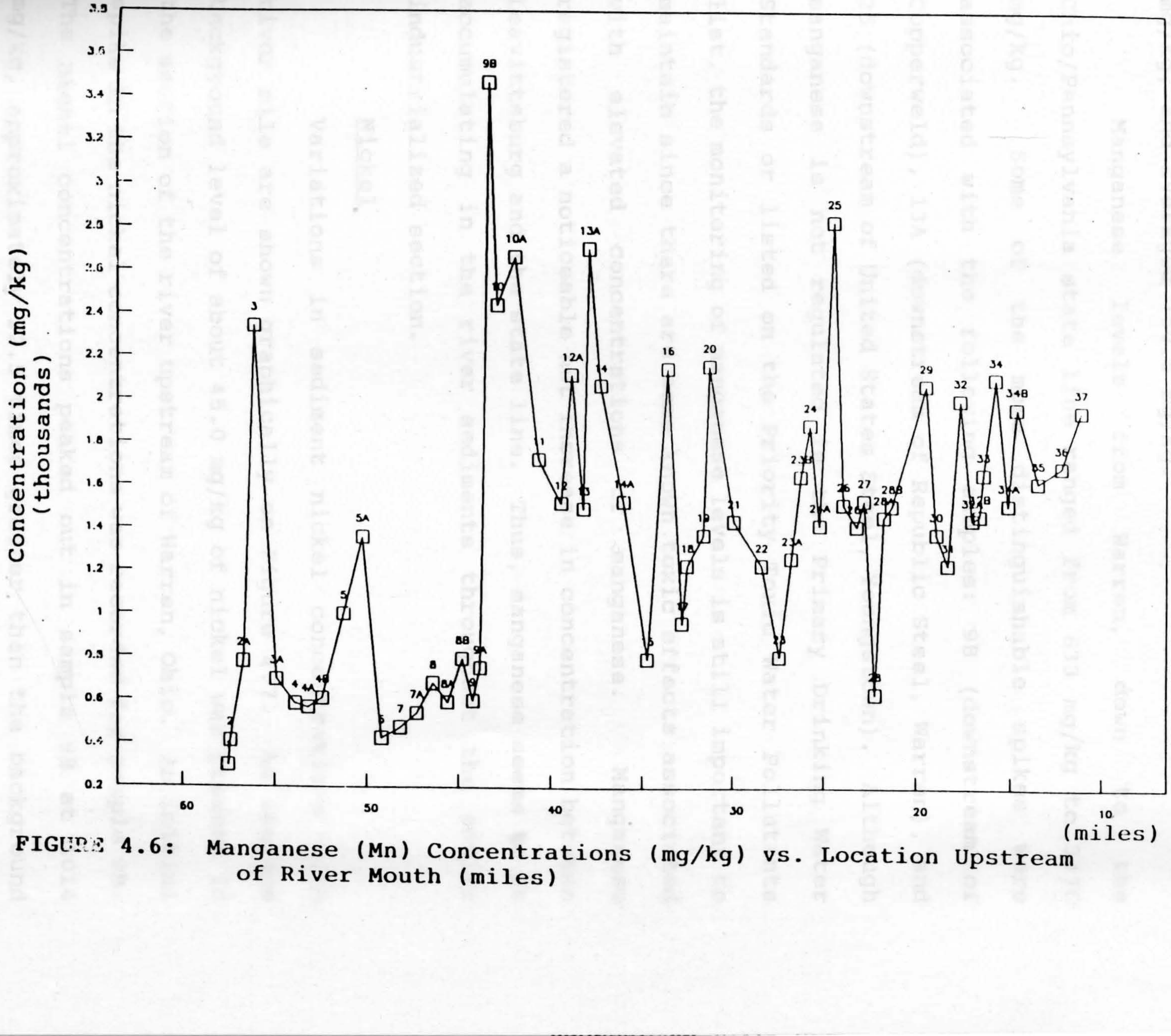


FIGURE 4.6: Manganese (Mn) Concentrations (mg/kg) vs. Location Upstream of River Mouth (miles)

manganese concentrations found between Newton Falls and Warren (samples 1 through 9) covered a range of 298 mg/kg to 2344 mg/kg, and averaged 750.5 mg/kg.

Manganese levels from Warren, down to the Ohio/Pennsylvania state line ranged from 633 mg/kg to 3470 mg/kg. Some of the more distinguishable spikes were associated with the following samples: 9B (downstream of Copperweld), 13A (downstream of Republic Steel, Warren), and 25 (downstream of United States Steel, Youngstown). Although manganese is not regulated in the Primary Drinking Water Standards or listed on the Priority Toxic Water Pollutants list, the monitoring of manganese levels is still important to maintain since there are some known toxic effects associated with elevated concentrations of manganese. Manganese registered a noticeable net increase in concentration between Leavittsburg and the state line. Thus, manganese seems to be accumulating in the river sediments throughout the entire industrialized section.

Nickel

Variations in sediment nickel concentrations with river mile are shown graphically on Figure 4.7. An average background level of about 45.0 mg/kg of nickel was present in the section of the river upstream of Warren, Ohio. An initial spike in the nickel concentrations was recorded for sample 9B. The nickel concentrations peaked out in sample 9B at 1014 mg/kg, approximately 22.5 times greater than the background

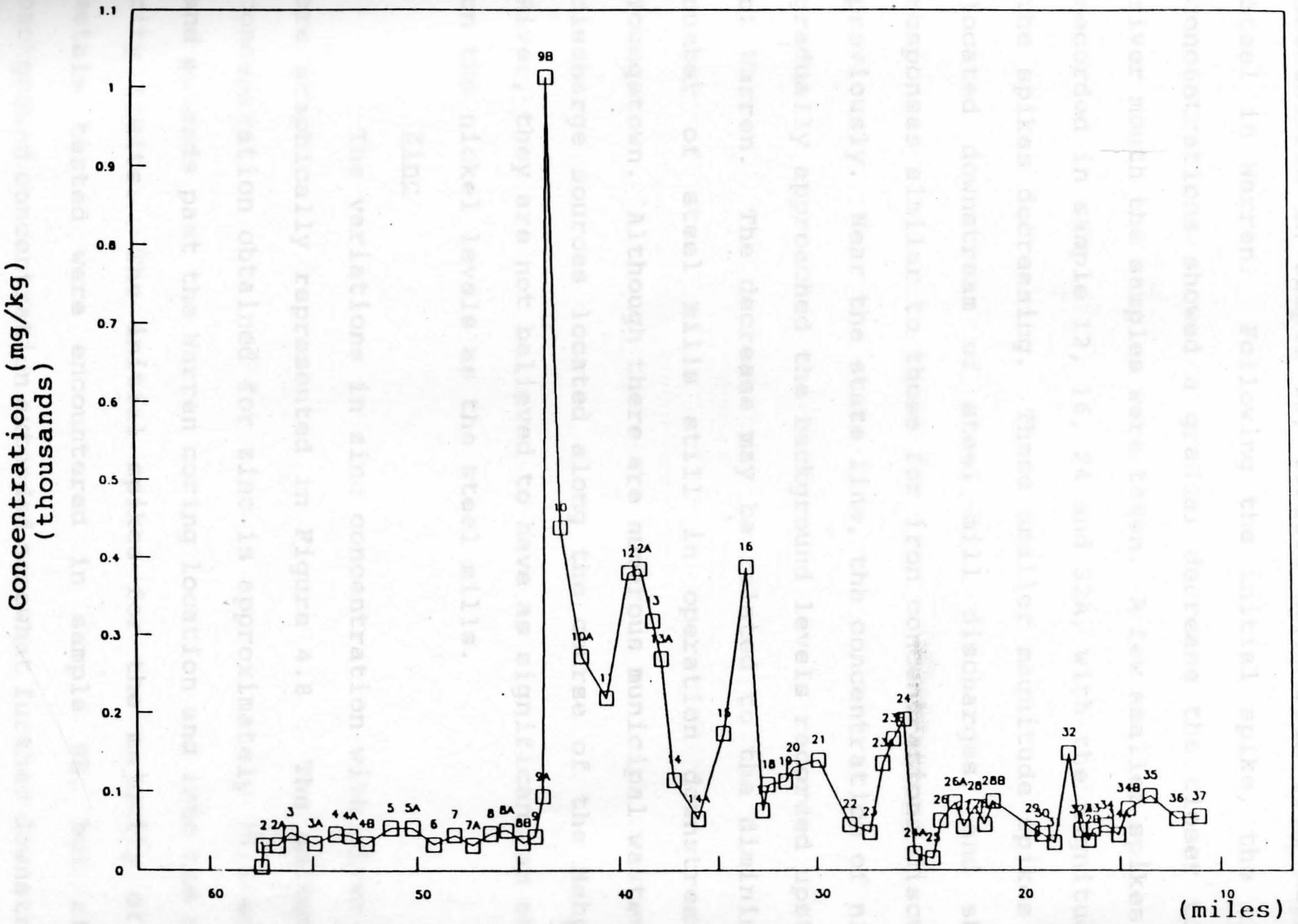


FIGURE 4.7: Nickel (Ni) Concentrations (mg/kg) vs. Location Upstream of River Mouth (miles)

concentration. The initial spike encountered in sample 9B was also 2.5 times higher than the second largest spike encountered in sample 16, located downstream from Republic Steel in Warren. Following the initial spike, the nickel concentrations showed a gradual decrease the closer to the river mouth the samples were taken. A few smaller spikes were recorded in sample 12, 16, 24 and 32A, with the magnitude of the spikes decreasing. These smaller magnitude spikes were located downstream of steel mill discharges, and showed responses similar to those for iron concentrations discussed previously. Near the state line, the concentration of nickel gradually approached the background levels recorded upstream of Warren. The decrease may be related to the diminishing number of steel mills still in operation downstream of Youngstown. Although there are numerous municipal wastewater discharge sources located along the course of the Mahoning River, they are not believed to have as significant an effect on the nickel levels as the steel mills.

Zinc

The variations in zinc concentration with river mile are graphically represented in Figure 4.8 The background concentration obtained for zinc is approximately 75.0 mg/kg, and extends past the Warren coring location and into the Niles city limits. The initial spikes for the majority of the metals tested were encountered in sample 9B, but zinc's background concentration extended somewhat further downstream.

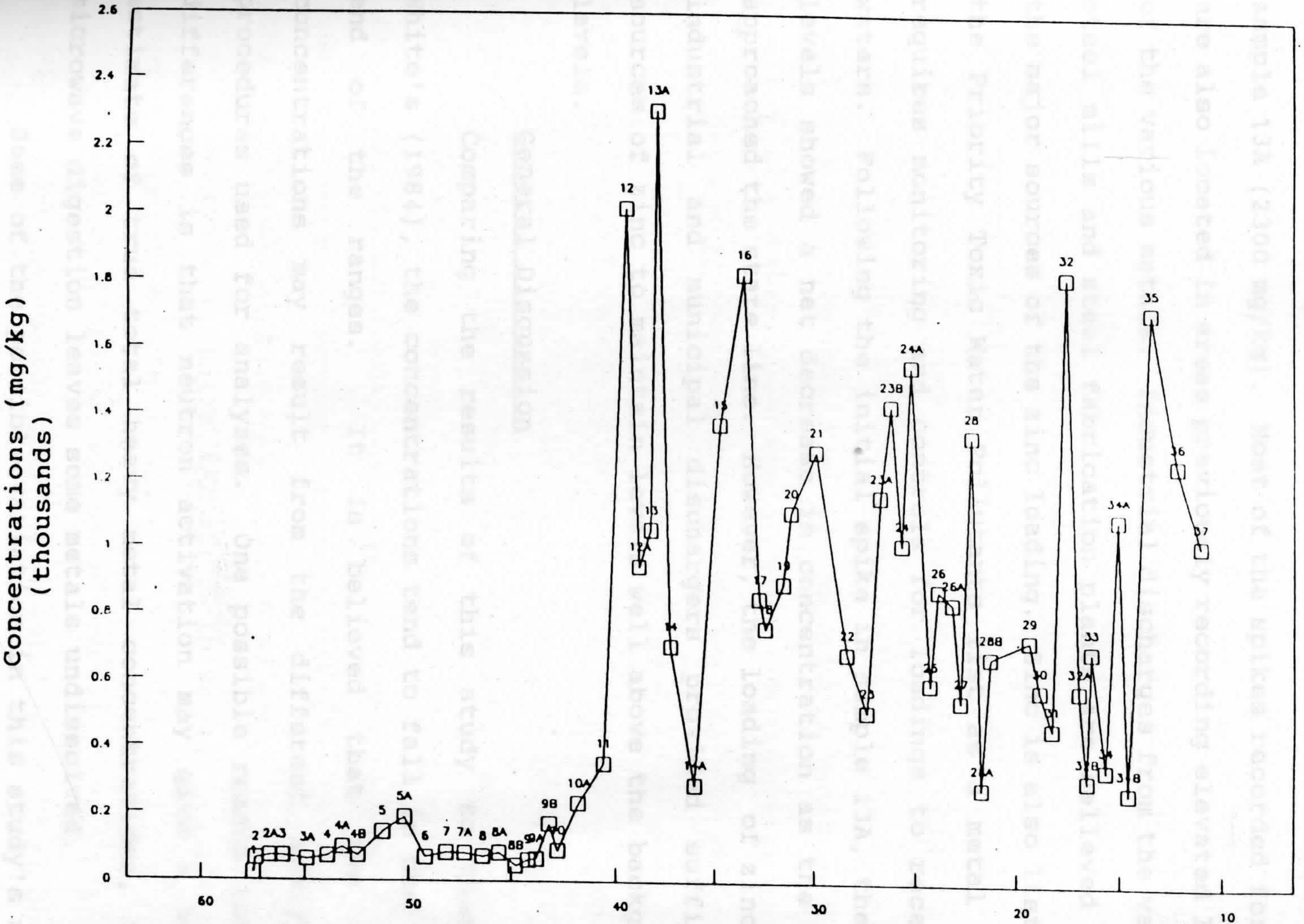


FIGURE 4.8: Zinc (Zn) Conecntrations (mg/kg) vs. Location Upstream of River Mouth (miles)

The first spike recorded for zinc was in sample 12 (2020 mg/kg), and is approximately 4.0 miles downstream from the Copperweld discharge. The maximum zinc level was recorded in sample 13A (2300 mg/kg). Most of the spikes recorded for zinc are also located in areas previously recording elevated levels of the various metals. Industrial discharges from the various steel mills and steel fabrication plants are believed to be the major sources of the zinc loading. Zinc is also listed on the Priority Toxic Water Pollutants list as a metal which requires monitoring and controls for loadings to receiving waters. Following the initial spike in sample 13A, the zinc levels showed a net decrease in concentration as the river approached the state line. However, the loading of zinc from industrial and municipal dischargers provided sufficient sources of zinc to maintain levels well above the background levels.

General Discussion

Comparing the results of this study to those of White's (1984), the concentrations tend to fall in the lower end of the ranges. It is believed that the lower concentrations may result from the different analytical procedures used for analyses. One possible reason for the differences is that neutron activation may give a better estimate of true total heavy metal concentrations, while microwave digestion leaves some metals undissolved.

Some of the possible variation in this study's metal concentrations may be attributed to the particle size distribution of the grab samples. Two samples taken from the same location will show variation in metal levels if one sample has a sandy composition and the other sample has a silty composition. The silty sample would typically record a higher concentration due to the larger surface area per unit sediment mass associated with the sample. Either on a per unit volume or per unit weight basis, a silty sample would provide more surface sites for the dissolved metal ions to adsorb to than would the sample with the sandy composition.

Although the particle size distribution for each grab sample was not recorded, a silty composition was consistently noticed in a majority of the samples. The similar particle size consistency resulted from taking most of the grab samples from the river banks. Only two or three grab samples were actually taken from the river's channel, and the compositions were typically more coarse, but still provided sufficient surface sites for metal adsorption to occur. The majority of the center river channel was extremely rocky and contained larger pebbles and rocks, requiring that grab samples be taken from the banks. Because sediment texture was reasonably consistent among samples, it is believed that the results are truly representive of the variation in metal concentrations along the length of the river.

Another possible source of variation in the metal levels may be the experimental procedures used in the sample analysis. The samples which were taken during the core sampling trips were analyzed at different times, while the remaining grab samples were all analyzed on the same day. Although all the samples were analyzed at the same wavelength for one particular metal, the AA could have varied in measured adsorption due to slight variations in the initial optimization of the flame analyzer.

As with any analytical procedure, there exists a margin for human error. But the percent difference which could have resulted from these possible errors is believed to be small, not causing any large errors within the analyses performed. Thus, the results are felt to be valid and accurate in representing the metal concentrations which occur along the length of the Mahoning River.

Core Samples

The analytical results from the core samples taken at the Leavittsburg, Warren, Youngstown and Struthers locations are listed in Tables 4.2 through 4.13, and presented graphically in Figure 4.9 through Figure 4.96. The graphs representing the core samples show that each metal behaves differently with almost every core sample taken. Each core heavy metal profile was classified as decreasing toward the sediment-water interface (DC), increasing toward the sediment-water interface (IC), or showing no distinct trend (NT). The results are summarized in Table 4.13.

TABLE 4.2: Metal Concentrations (mg/kg) vs. Depth (inches) for the Left Bank Core Taken at the Warren Coring Site

SAMPLE NAME	Manganese Mn (mg/kg)	Copper Cu (mg/kg)	Zinc Zn (mg/kg)	Cadmium Cd (mg/kg)	Nickel Ni (mg/kg)	Lead Pb (mg/kg)	Chromium Cr (mg/kg)	Iron Fe (mg/kg)
LZ-LB1	4700	0	210	7.1	1203	871	1317	288100
LZ-LB2	3160	435	326	4.6	747	306	681	203400
LZ-LB3	3760	680	322	6	850	234	640	244700
LZ-LB4	4630	961	185	7	1155	239	1031	289500
LZ-LB5	3810	646	190	5.4	856	170	392	144600
LZ-LB6	4430	643	257	6.6	1035	197	566	189000
LZ-LB7	4790	362	193	4.6	1132	147	600	160900
LZ-LB8	4740	491	335	6.3	809	206	364	189200
LZ-LB9	4660	270	162	4.3	1586	158	727	147600
LZ-LB10	2330	329	87	5	2269	345	1228	222300
LZ-LB11	2630	270	126	4.6	2386	276	1209	199400
LZ-LB12	2500	161	158	3.5	1356	165	820	136900
LZ-LB13	1780	168	153	4.1	1170	196	1093	151500

TABLE 4.3: Metal Concentrations (mg/kg) vs. Depth (inches) for the Left Channel Core Taken at the Warren Coring Site

SAMPLE NAME	Manganese Mn (mg/kg)	Copper Cu (mg/kg)	Zinc Zn (mg/kg)	Cadmium Cd (mg/kg)	Nickel Ni (mg/kg)	Lead Pb (mg/kg)	Chromium Cr (mg/kg)	Iron Fe (mg/kg)
LZ-LC1	4610	549	1680	6.4	848	221	579	194500
LZ-LC2	4320	514	1820	6.2	778	221	471	183900
LZ-LC3	4540	696	2130	7.2	963	253	729	244800
LZ-LC4	4290	786	312	7.3	1320	239	864	292900
LZ-LC5	4130	631	208	5.7	1646	230	709	217000
LZ-LC6	1770	349	97400	7.8	277	623	494	182100
LZ-LC7	4540	883	252	7.2	1088	292	915	261000
LZ-LC8	4700	314	150	4.4	2307	151	359	171700

TABLE 4.4: Metal Concentrations (mg/kg) vs. Depth (inches) for the Left Channel Core Taken at the Newton Falls Coring Site

SAMPLE NAME	Manganese Mn (mg/kg)	Copper Cu (mg/kg)	Zinc Zn (mg/kg)	Cadmium Cd (mg/kg)	Nickel Ni (mg/kg)	Lead Pb (mg/kg)	Chromium Cr (mg/kg)	Iron Fe (mg/kg)
NF-LC1	1130	25.3	157	2	42	51	28	32320
NF-LC2	840	27.9	150	2.2	45	53	20	34000
NF-LC3	3230	28.2	170	2.1	4.5	59	25	36200
NF-LC4	1130	25.5	173	2	44	56	21	32500
NF-LC5	1010	29	173	2.3	46	53	20	34300
NF-LC6	848	25.9	145	2.2	46	56	27	34800
NF-LC7	4880	26.1	144	2	44	56	25	34400
NF-LC8	1580	27.4	172	2.1	42	60	29	36400

TABLE 4.5: Metal Concentrations (mg/kg) vs. Depth (inches) for the Left Bank Core Taken at the Newton Falls Coring Site

SAMPLE NAME	Manganese Mn (mg/kg)	Copper Cu (mg/kg)	Zinc Zn (mg/kg)	Cadmium Cd (mg/kg)	Nickel Ni (mg/kg)	Lead Pb (mg/kg)	Chromium Cr (mg/kg)	Iron Fe (mg/kg)
NF-LB1	998	22.2	122	2.2	37	48	21	29300
NF-LB2	1120	27.3	171	2.4	49	61	26	39100
NF-LB3	1130	26.3	161	2.4	48	61	25	38100
NF-LB4	1430	26.3	160	2.2	47	63	27	39100
NF-LB5	1500	26	157	2.3	47	60	27	38500
NF-LB6	1670	28.1	165	2.3	47	73	27	38800
NF-LB7	925	20.1	121	1.7	36	47	20	28600
NF-LB8	937	25.3	149	2.3	44	58	23	35600
NF-LB9	928	26.9	152	2.2	47	61	25	38100
NF-LB10	913	25	150	2.2	43	56	16	35600
NF-LB11	912	26.1	154	2.5	43	58	18	36300
NF-LB12	1000	24.1	165	2.4	39	53	23	34500
NF-LB13	812	26.4	154	2.4	40	51	18	32700
NF-LB14	1920	26.7	190	2.4	39	55	26	36400

TABLE 4.6: Metal Concentrations (mg/kg) vs. Depth (inches) for the Right Channel Core Taken at the Newton Falls Coring Site

SAMPLE NAME	Manganese Mn (mg/kg)	Copper Cu (mg/kg)	Zinc Zn (mg/kg)	Cadmium Cd (mg/kg)	Nickel Ni (mg/kg)	Lead Pb (mg/kg)	Chromium Cr (mg/kg)	Iron Fe (mg/kg)
NF-RC1	687	4.9	32	0.7	7	18	12	6200
NF-RC2	2550	18	85	1.5	24	35	16	18900
NF-RC3	3170	0.3	62	1.3	15	25	11	13600
NF-RC4	638	4.4	43	0.9	6	16	6	6300
NF-RC5	378	7.9	59	1.4	14	32	12	12900
NF-RC6	969	2.1	29	0.8	5	29	5	6700

TABLE 4.7: Metal Concentrations (mg/kg) vs. Depth (inches) for the Right Bank Core Taken at the Newton Falls Coring Site

SAMPLE NAME	Manganese Mn (mg/kg)	Copper Cu (mg/kg)	Zinc Zn (mg/kg)	Cadmium Cd (mg/kg)	Nickel Ni (mg/kg)	Lead Pb (mg/kg)	Chromium Cr (mg/kg)	Iron Fe (mg/kg)
NF-RB1								
NF-RB2	754	12.1	70	1.5	16	30	9	14900
NF-RB3	1230	22.1	126	2.3	38	58	19	29200
NF-RB4	851	16.9	92	1.7	29	45	12	19700
NF-RB5	1240	24.1	135	2.2	46	63	19	30700
NF-RB6	1750	16.1	89	1.5	20	42	15	18500
NF-RB7	1540	16.3	93	1.6	23	41	11	20000
NF-RB8	1720	17	83	1.5	17	38	8	16800
NF-RB9	2240	19.1	82	1.5	18	33	11	17500
NF-RB10	1730	16.2	84	1.6	18	34	10	17000
NF-RB11	1740	8.9	48	1.1	10	21	3	10000
NF-RB12	956	2.1	43	1.1	5	19	6	10000

TABLE 4.8: Metal Concentrations (mg/kg) vs. Depth (inches) for the Right Bank Core Taken at the Struthers Coring Site

SAMPLE NAME	Manganese Mn (mg/kg)	Copper Cu (mg/kg)	Zinc Zn (mg/kg)	Cadmium Cd (mg/kg)	Nickel Ni (mg/kg)	Lead Pb (mg/kg)	Chromium Cr (mg/kg)	Iron Fe (mg/kg)
ST-RB200-1	1968	2342	2370	0	59.7	511	256	144800
ST-RB200-2	1840	2394	2885	0	61.5	583	271.6	147350
ST-RB200-3	1692	2390	3230	0	66.3	655	257.3	180800
ST-RB200-4	1457	2699	4625	0	137.5	1117	240.8	166600
ST-RB200-5	1448	3171	5750	0	196.7	1600	302	170750
ST-RB200-6	1213	3028	5840	0	165.9	1476	227.7	169250
ST-RB200-7	1009	2103	1760	0	55.2	239	219.5	93650
ST-RB200-8	1824	2608	3335	0	26.4	780	121.3	208900
ST-RB200-9	1721	2765	2915	0	22.2	717	104.9	209700
ST-RB200-10	1894	2506	1480	0	14.2	433	83.7	234000

TABLE 4.9: Metal Concentrations (mg/kg) vs. Depth (inches) for the Left Bank Core Taken at the Struthers Coring Site

SAMPLE NAME	Manganese Mn (mg/kg)	Copper Cu (mg/kg)	Zinc Zn (mg/kg)	Cadmium Cd (mg/kg)	Nickel Ni (mg/kg)	Lead Pb (mg/kg)	Chromium Cr (mg/kg)	Iron Fe (mg/kg)
ST-LB1	1773	2127	3785	0	32.1	250	110.8	175100
ST-LB2	2183	2182	775	0	29.4	217	124.6	221700
ST-LB3	2567	2180	456	0	32.3	406	220.3	136550
ST-LB4	2378	2132	515	0	32.1	449	224.5	92600
ST-LB5	2502	2159	900	0	36.1	509	241.1	156300
ST-LB6	2865	2228	479	0	45.2	504	275.6	98650
ST-LB7	2369	2065	378	0	34.6	445	209.5	88600
ST-LB8	2232	2074	365	0	36.6	430	210.8	104750
ST-LB9	2604	2195	330	0	39.4	411	203	167500
ST-LB10	2198	2228	461	0	42	437	184.1	187600

TABLE 4.10: Metal Concentrations (mg/kg) vs. Depth (inches) for the Right Bank Core Taken at the Struthers Coring Site

SAMPLE NAME	Manganese Mn (mg/kg)	Copper Cu (mg/kg)	Zinc Zn (mg/kg)	Cadmium Cd (mg/kg)	Nickle Ni (mg/kg)	Lead Pb (mg/kg)	Chromium Cr (mg/kg)	Iron Fe (mg/kg)
ST-RB.75-1	1005	2405	826	0	105.9	734	317.5	159550
ST-RB.75-2	946	2512	884	0	124	794	312.3	155450
ST-RB.75-3	1143	2497	941	0	109	827	368.9	165350
ST-RB.75-4	747	2502	931	0	111.4	873	381.3	159300
ST-RB.75-5	722	2370	815	0	110.9	724	330	139250
ST-RB.75-6	671	2451	466	0	87	529	202.2	173450
ST-RB.75-7	317	2556	340	0	89.1	486	133.5	215100
ST-RB.75-8	1101	2495	286	0	99.6	409	139.7	210050

TABLE 4.11: Metal Concentrations (mg/kg) vs. Depth (inches) for the Center Channel Core Taken at the Youngstown Coring Site

SAMPLE NAME	Manganese Mn (mg/kg)	Copper Cu (mg/kg)	Zinc Zn (mg/kg)	Cadmium Cd (mg/kg)	Nickle Ni (mg/kg)	Lead Pb (mg/kg)	Chromium Cr (mg/kg)	Iron Fe (mg/kg)
Y-CCH1	2392	2082	1365	3.3	119.4	428	165.7	253800
Y-CCH2	2349	1920	625	2.8	79.9	249	133.7	227700
Y-CCH3	2693	2120	345	2.1	91.7	238	129.6	297650
Y-CCH4	2578	1984	675	1.5	82.1	243	94.7	220200
Y-CCH5	2800	1995	675	2.7	85.7	317	128.2	289350
Y-CCH6	3192	1901	700	0	78.1	287	118.7	300450

TABLE 4.12: Metal Concentrations (mg/kg) vs. Depth (inches) for the Left Bank Core Taken at the Youngstown Coring Site

SAMPLE NAME	Manganese Mn (mg/kg)	Copper Cu (mg/kg)	Zinc Zn (mg/kg)	Cadmium Cd (mg/kg)	Nickle Ni (mg/kg)	Lead Pb (mg/kg)	Chromium Cr (mg/kg)	Iron Fe (mg/kg)
Y-LB.25-1	1571	1645	795	0	60.5	270	104.5	204650
Y-LB.25-2	2149	1625	568	0	49	388	88.9	93450
Y-LB.25-3	2134	1623	1002	0	60.7	449	132.8	81150
Y-LB.25-4	1031	1681	938	0	63.8	430	120.4	90150
Y-LB.25-5	1765	1653	918	0	67.7	465	138.4	77200
Y-LB.25-6	1318	1624	1139	0	79.5	446	130	63600
Y-LB.25-7	961	1616	1354	0	97.6	420	172.8	59750
Y-LB.25-8	849	1532	1136	0	86.4	324	159.2	73000
Y-LB.25-9	967	1573	1486	0	101.3	364	187.3	86000

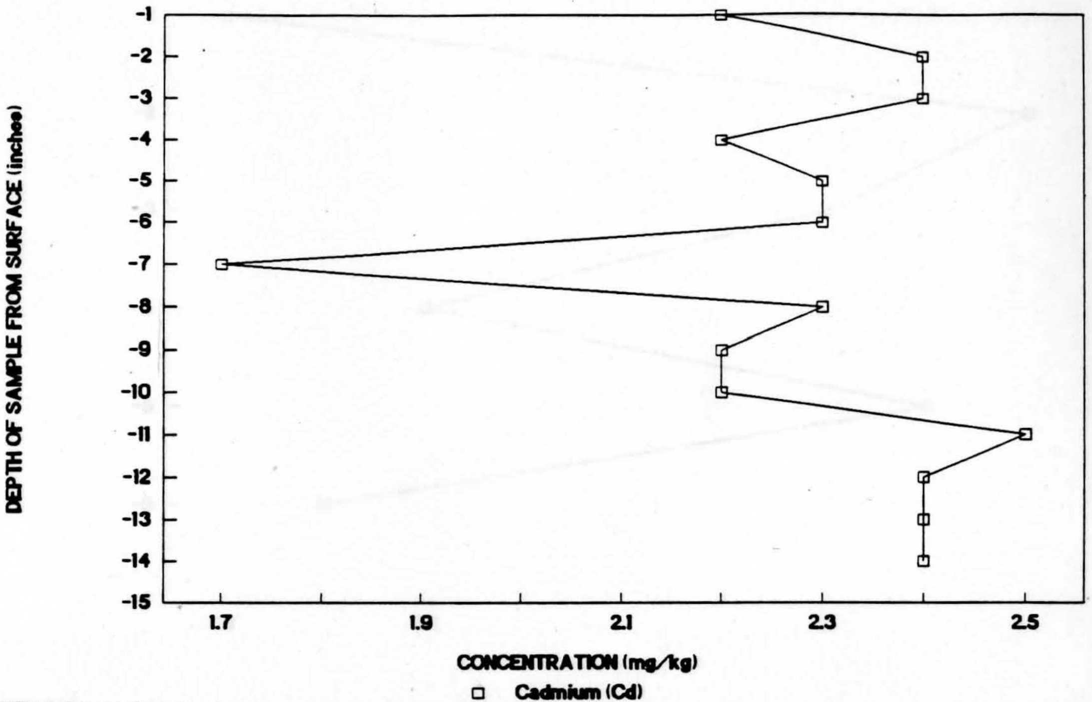


FIGURE 4.9: Cadmium Concentrations (mg/kg) Varying With Depth (inches) at the Newton Falls Coring Location (left bank, in vicinity of the Newton Falls water intake line)

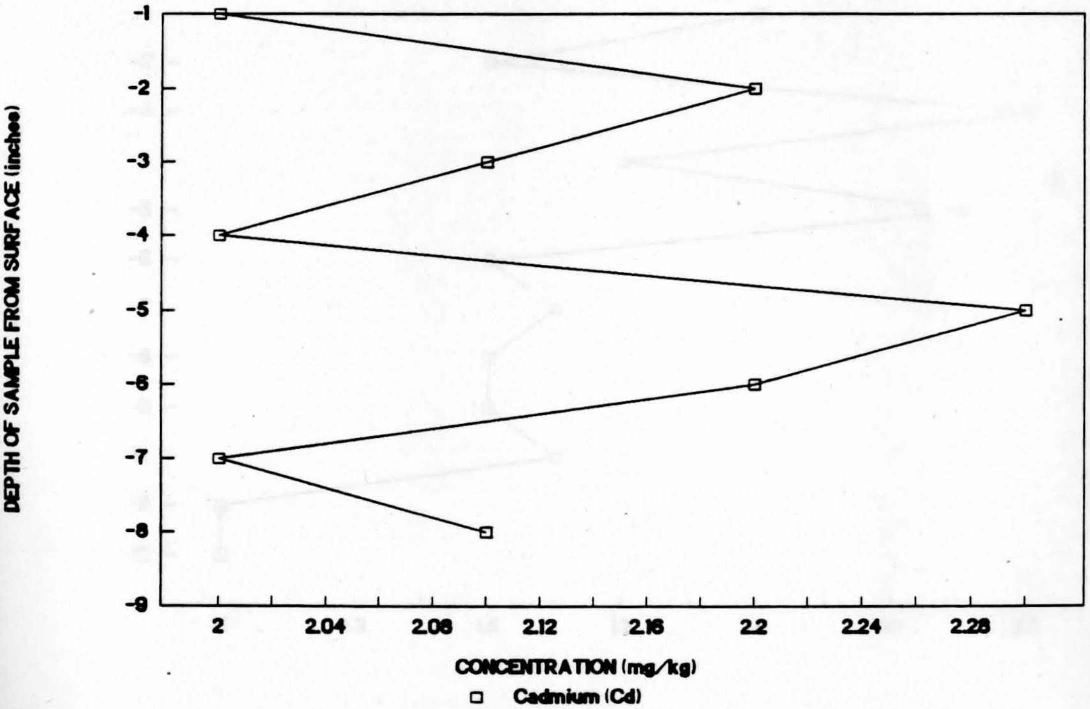


FIGURE 4.10: Cadmium Concentrations (mg/kg) Varying With Depth (inches) at the Newton Falls Coring Location (left channel, in vicinity of the Newton Falls water intake line)

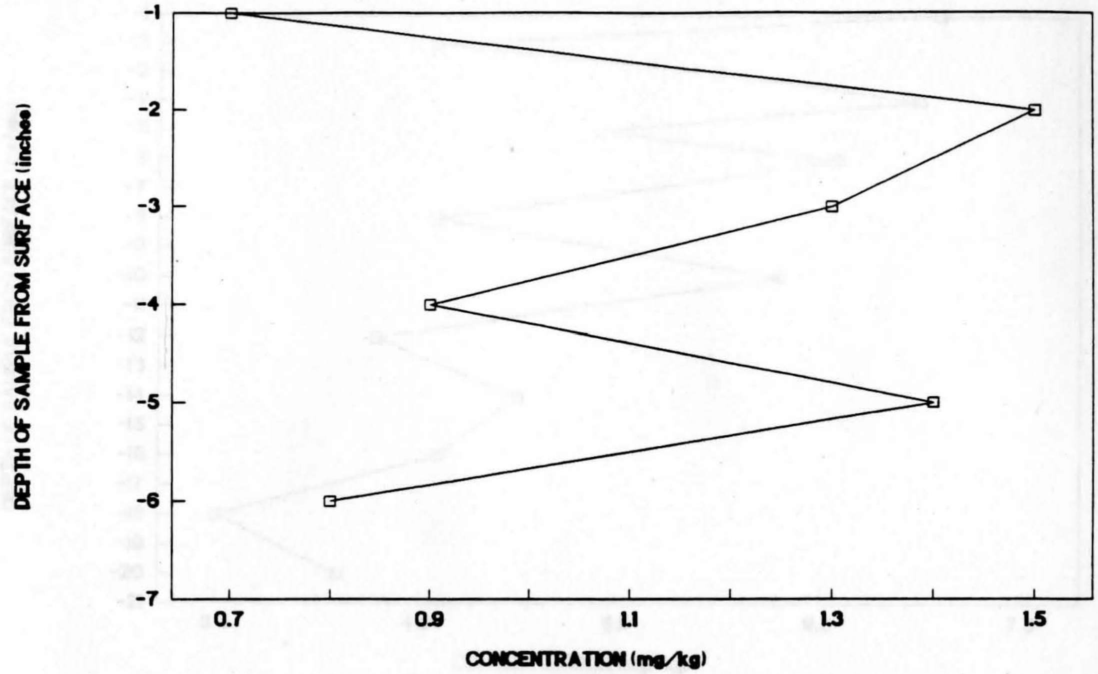


FIGURE 4.11: Cadmium Concentrations (mg/kg) Varying With Depth (inches) at the Newton Falls Coring Location (right channel, in vicinity of the Newton Falls water intake line)

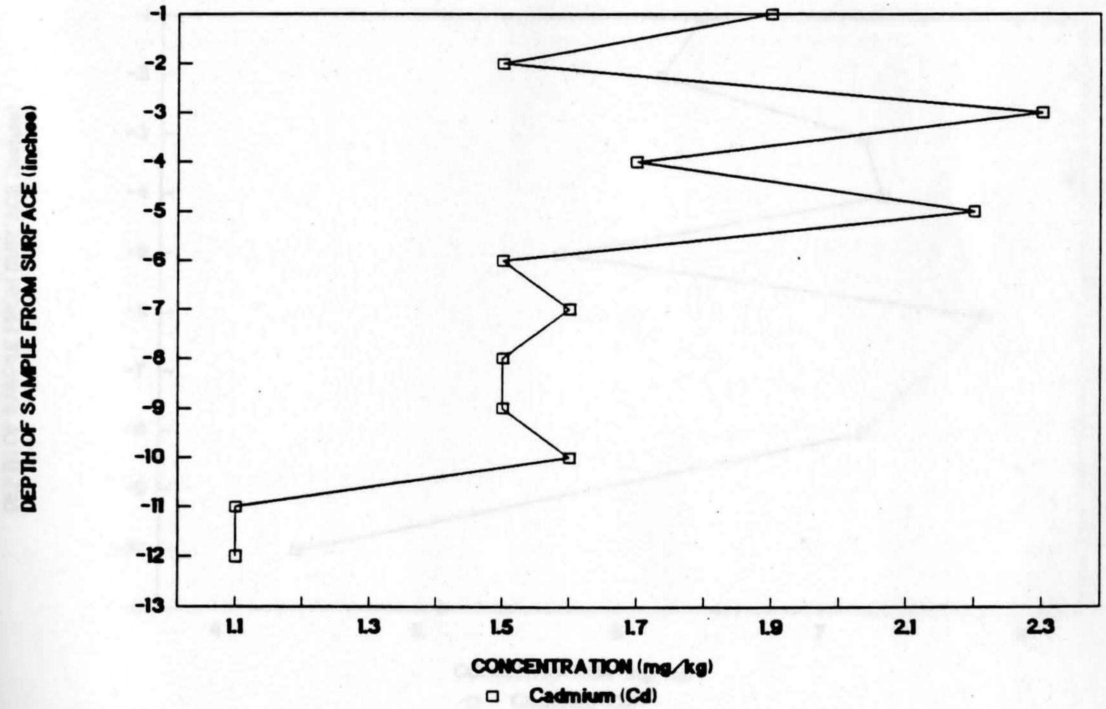


FIGURE 4.12: Cadmium Concentrations (mg/kg) Varying With Depth (inches) at the Newton Falls Coring Location (right bank, in vicinity of the Newton Falls water intake line)

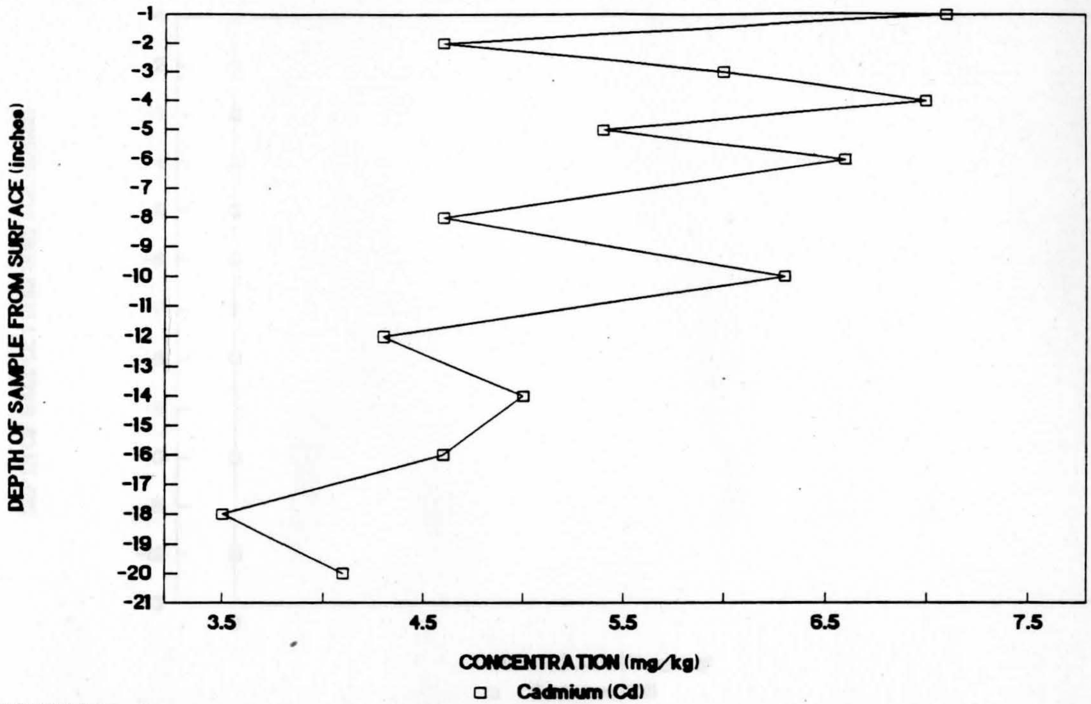


FIGURE 4.13: Cadmium Concentrations (mg/kg) Varying With Depth (inches) at the Warren Coring Location (left bank, directly downstream from the Copperweld discharge)

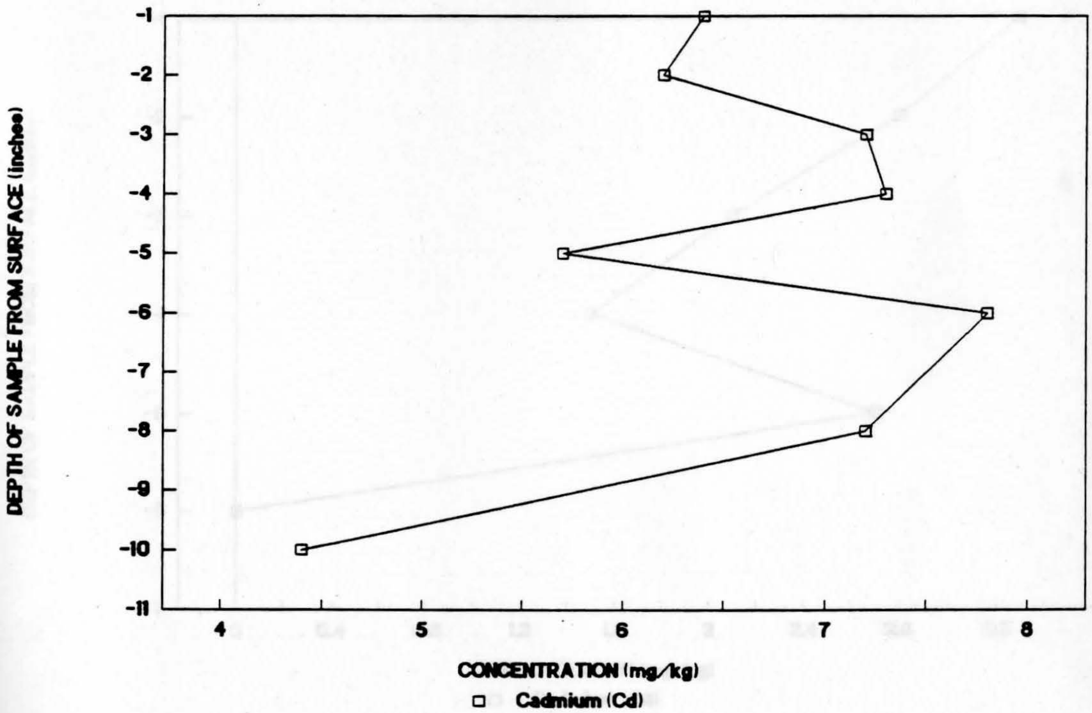


FIGURE 4.14: Cadmium Concentrations (mg/kg) Varying With Depth (inches) at the Warren Coring Location (right channel, directly downstream from the Copperweld discharge)

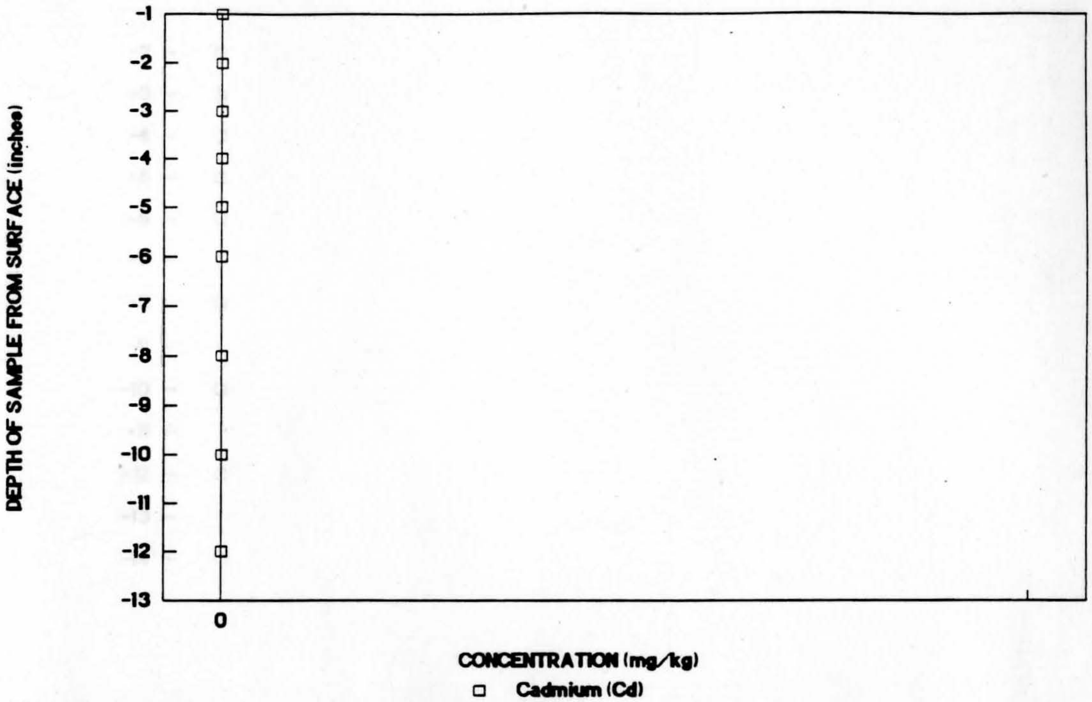


FIGURE 4.15: Cadmium Concentrations (mg/kg) Varying With Depth (inches) at the Youngstown Coring Location (left bank, 200 ft downstream from the Youngstown municipal discharge line)

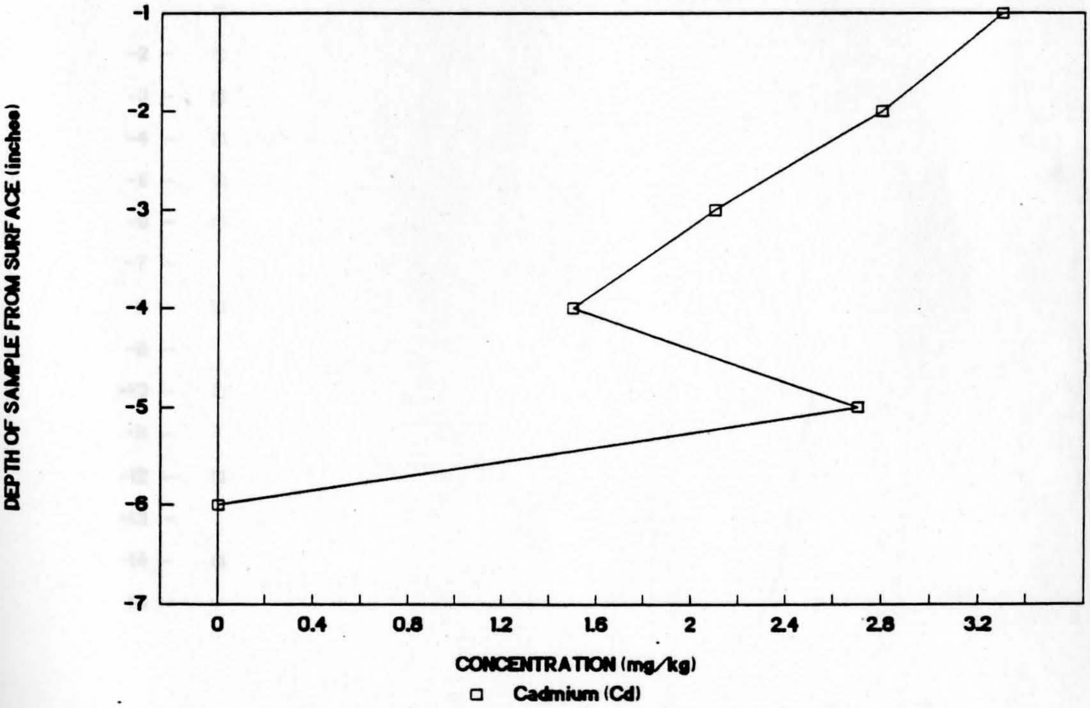


FIGURE 4.16: Cadmium Concentrations (mg/kg) Varying With Depth (inches) at the Youngstown Coring Location (center channel, a half mile downstream from the Youngstown municipal discharge)

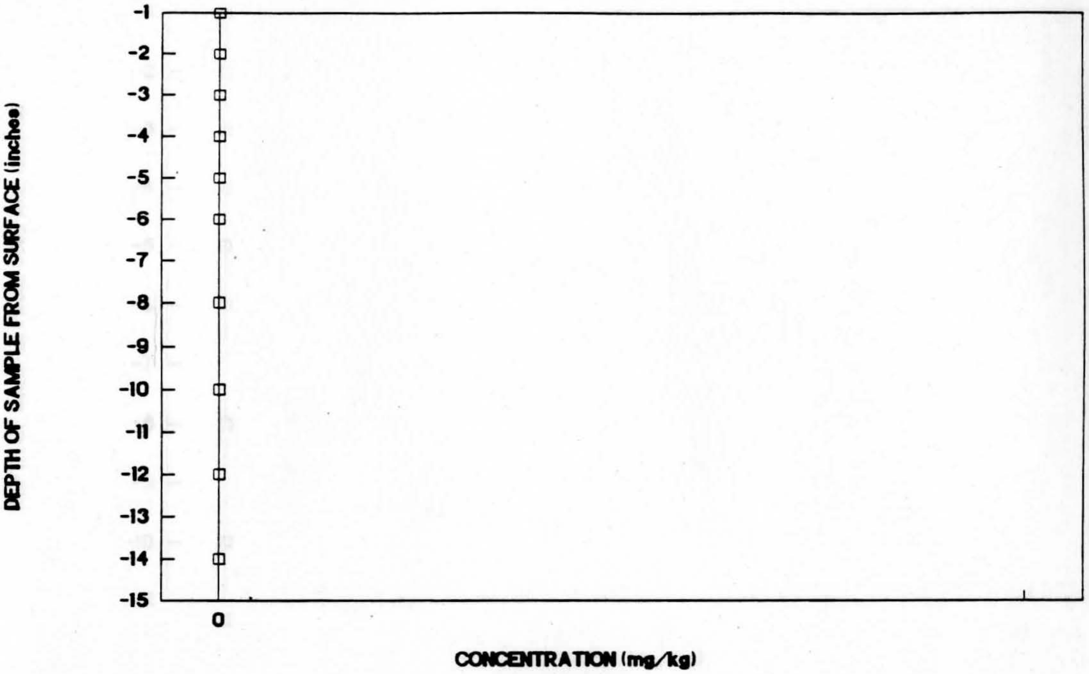


FIGURE 4.17: Cadmium Concentrations (mg/kg) Varying With Depth (inches) at the Struthers Coring Location (left bank, directly across from the Struthers municipal discharge culvert)

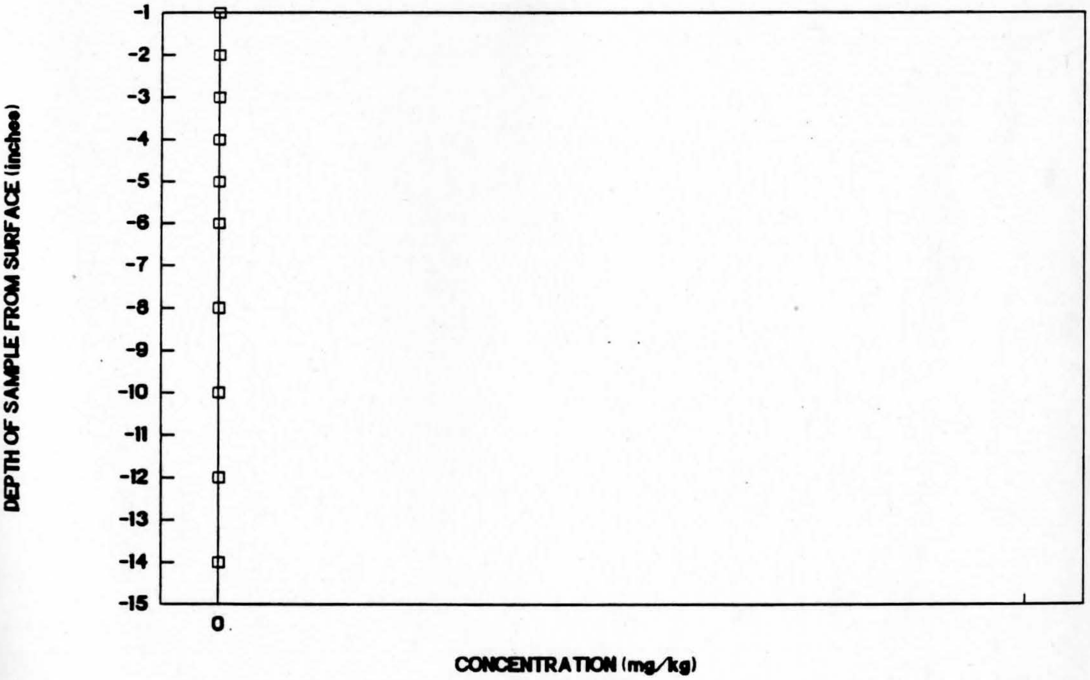


FIGURE 4.18: Cadmium Concentrations (mg/kg) Varying With Depth (inches) at the Struthers Coring Location (right bank, 200 ft downstream from the Struthers municipal discharge culvert)

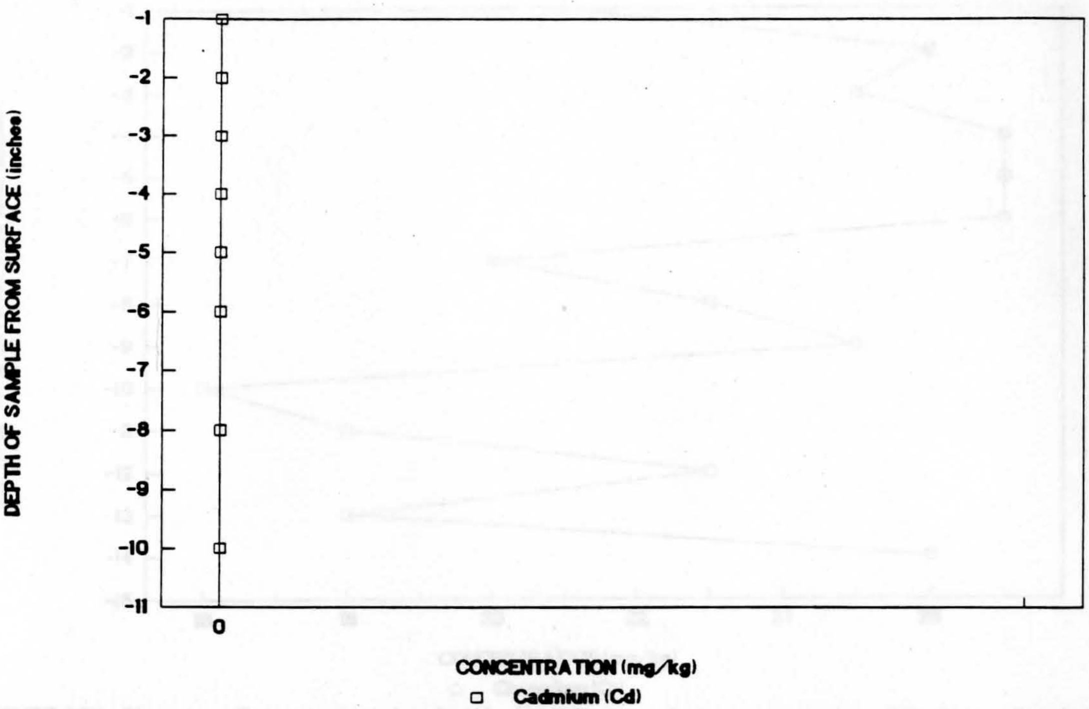


FIGURE 4.19: Cadmium Concentrations (mg/kg) Varying With Depth (inches) at the Struthers Coring Location (left bank, a quarter mile downstream from the Struthers municipal discharge culvert)

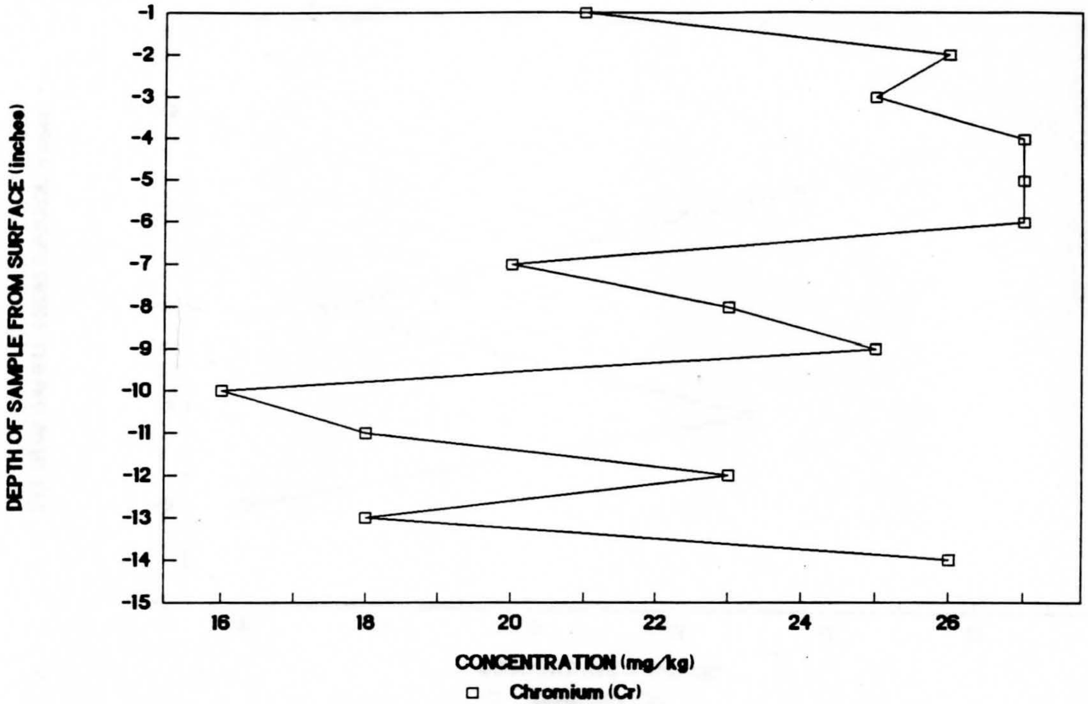


FIGURE 4.20: Chromium Concentrations (mg/kg) Varying With Depth (inches) at the Newton Falls Coring Location (left bank, in vicinity of the Newton Falls water intake line)

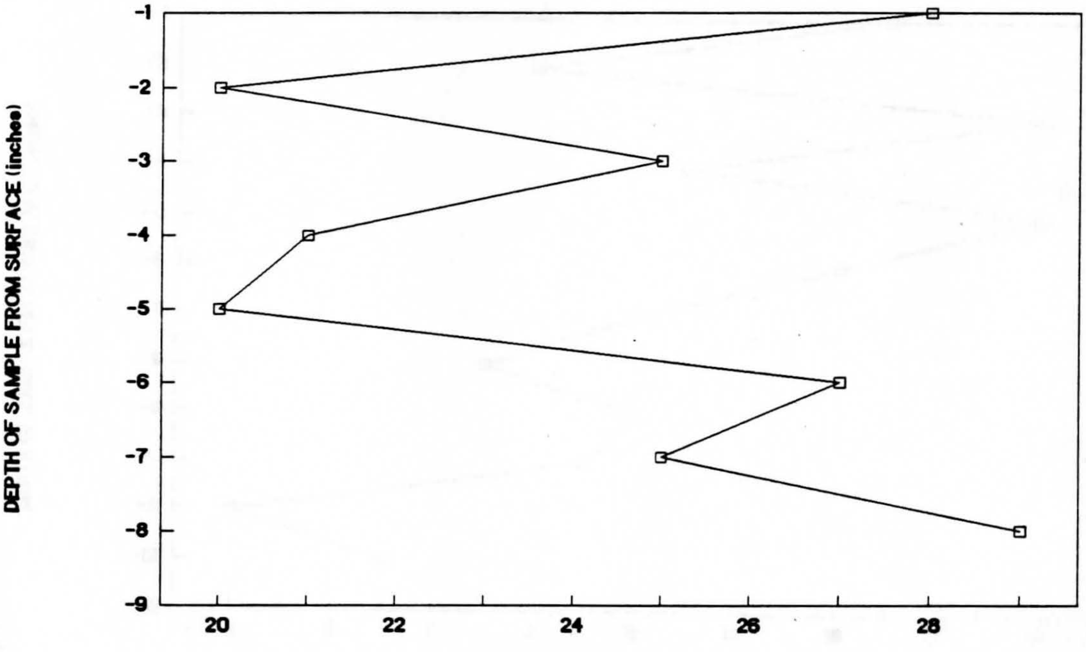


FIGURE 4.21: Chromium Concentrations (mg/kg) Varying With Depth (inches) at the Newton Falls Coring Location (left channel, in vicinity of the Newton Falls water intake line)

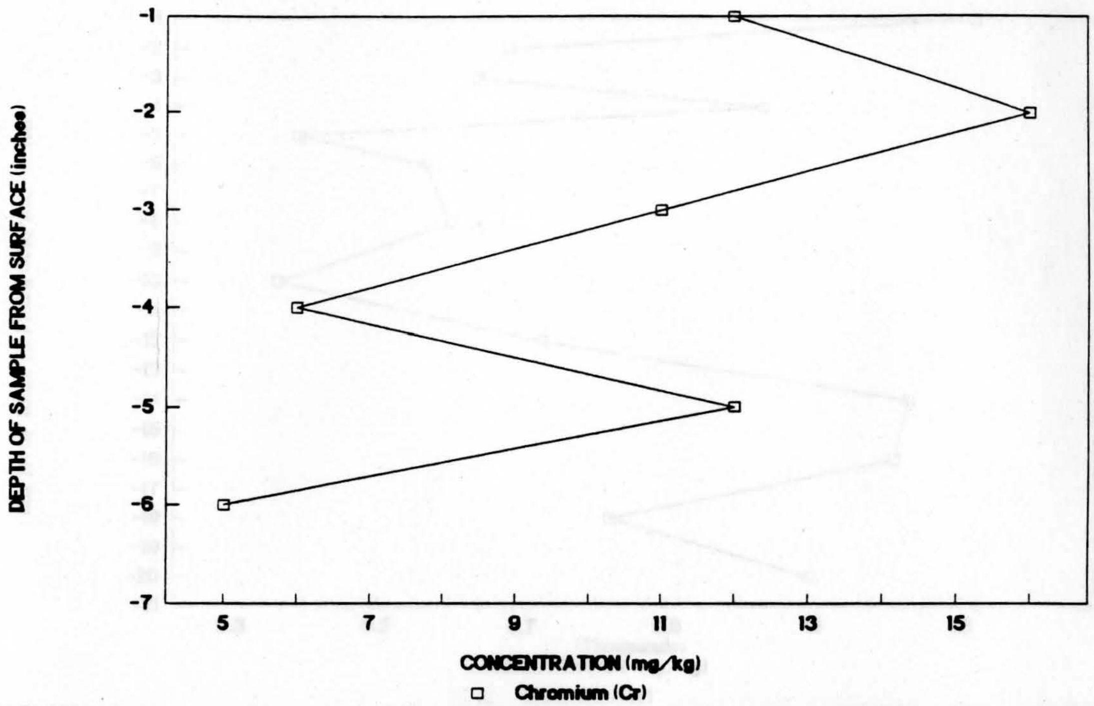


FIGURE 4.22: Chromium Concentrations (mg/kg) Varying With Depth (inches) at the Newton Falls Coring Location (right channel, in vicinity of the Newton Falls water intake line)

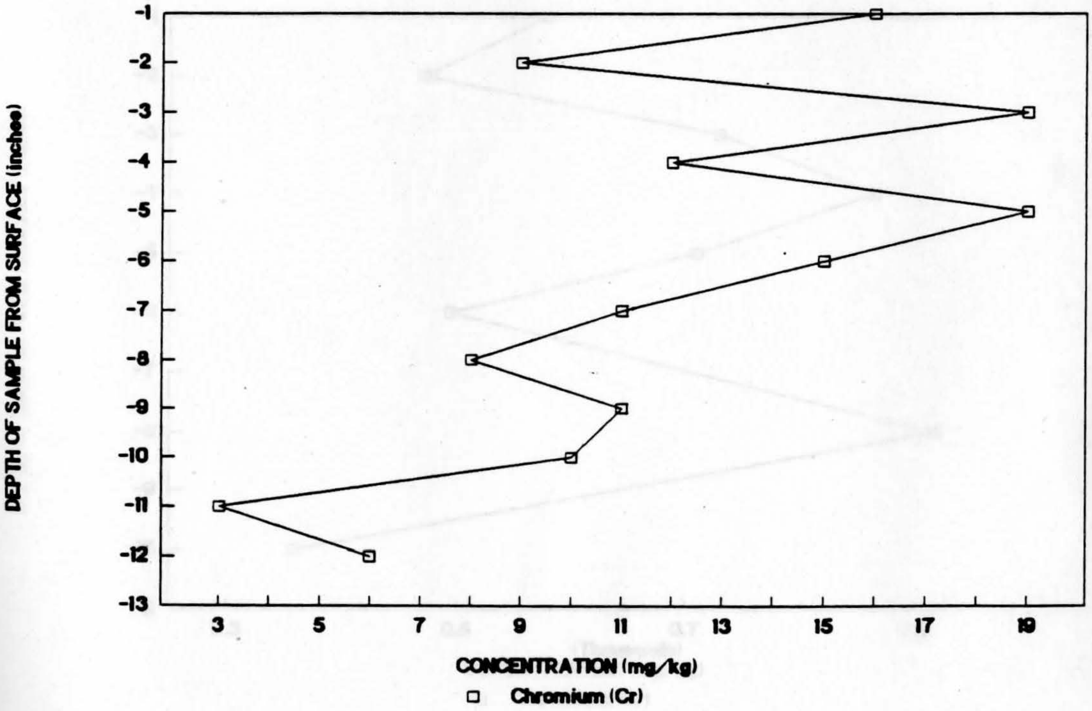


FIGURE 4.23: Chromium Concentrations (mg/kg) Varying With Depth (inches) at the Newton Falls Coring Location (right bank, in vicinity of the Newton Falls water intake line)

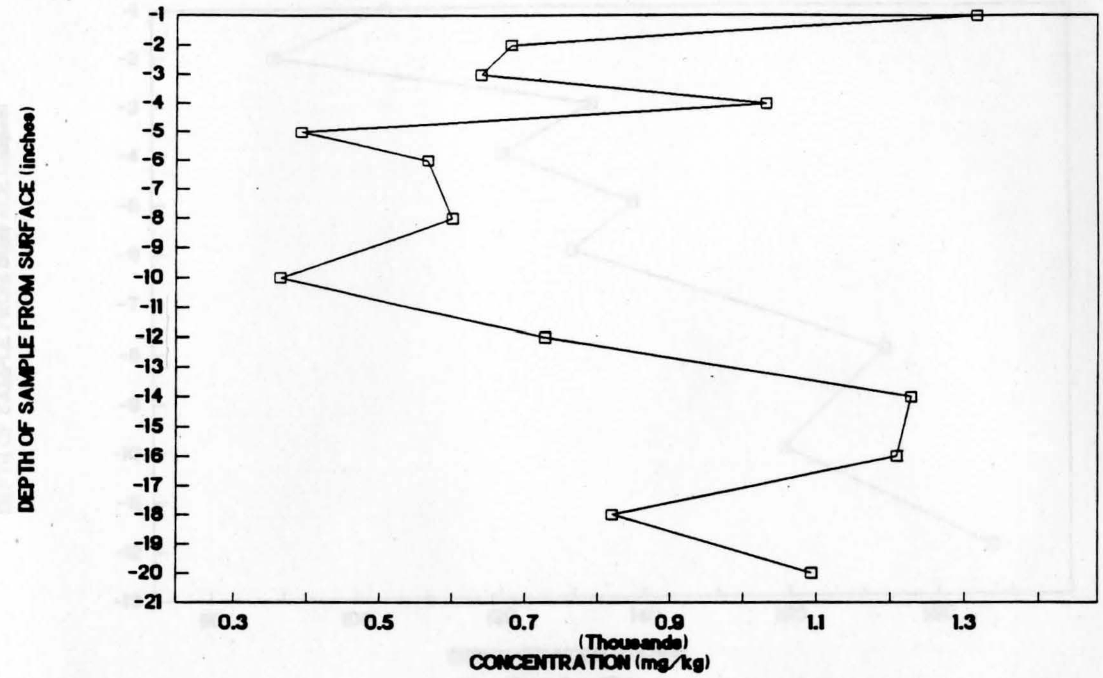


FIGURE 4.24: Chromium Concentrations (mg/kg) Varying With Depth (inches) at the Warren Coring Location (left bank, directly downstream from the Copperweld discharge)

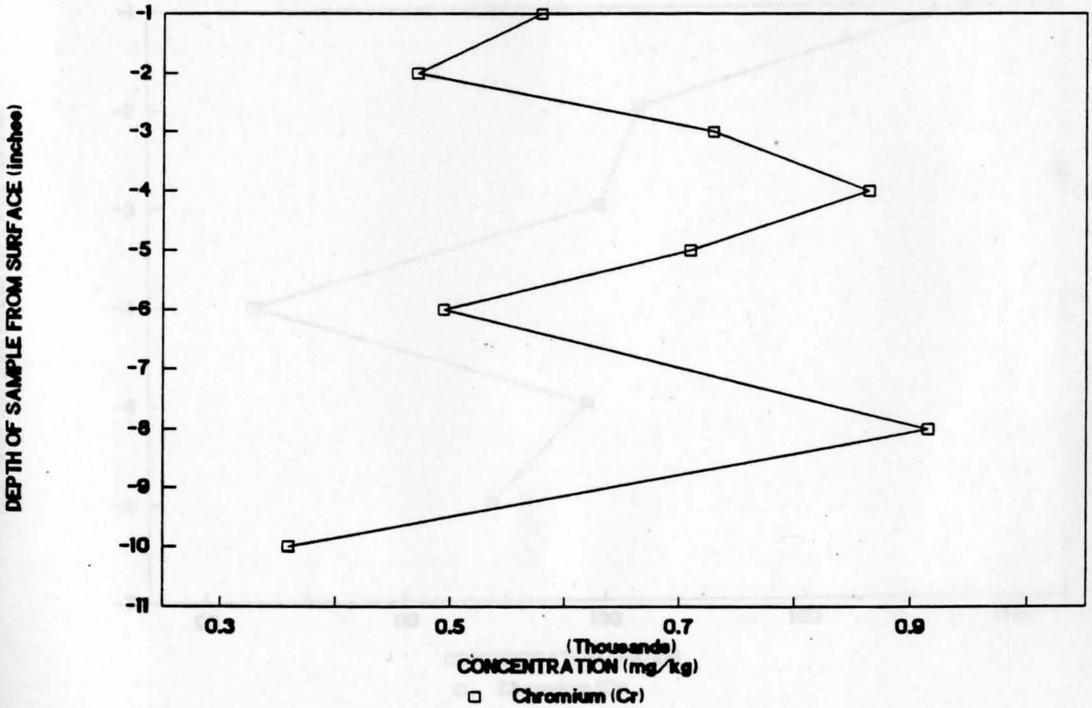


FIGURE 4.25: Chromium Concentrations (mg/kg) Varying With Depth (inches) at the Warren Coring Location (right channel, directly downstream from the Copperweld discharge)

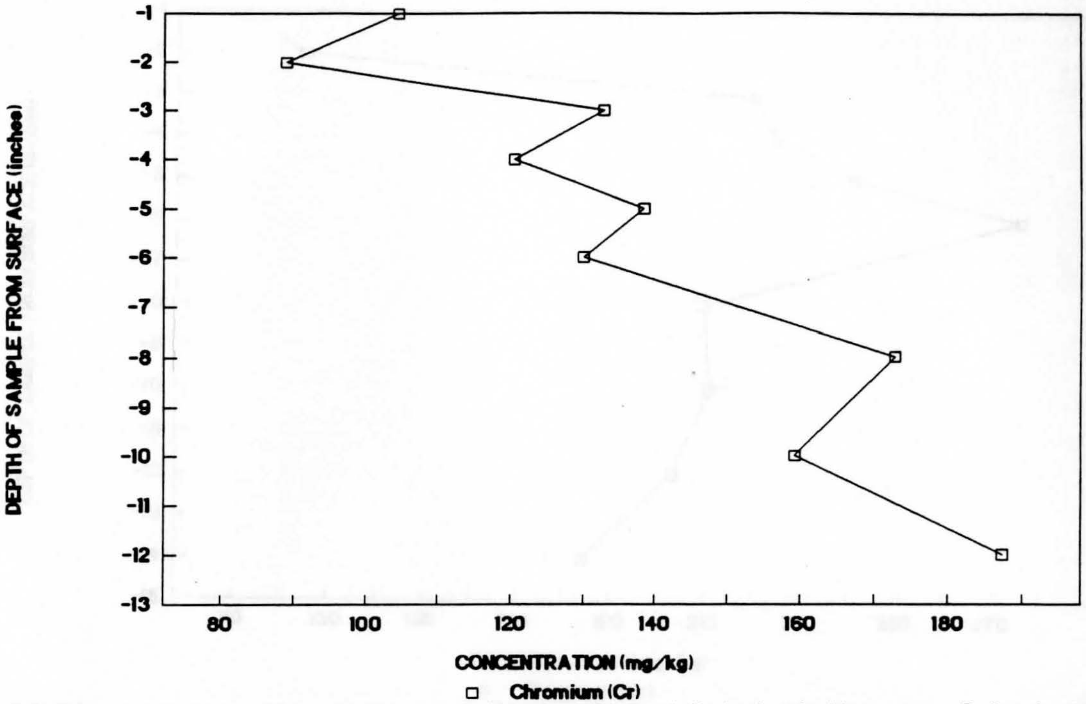


FIGURE 4.26: Chromium Concentrations (mg/kg) Varying With Depth (inches) at the Youngstown Coring Location (left bank, 200 ft downstream from the Youngstown municipal discharge line)

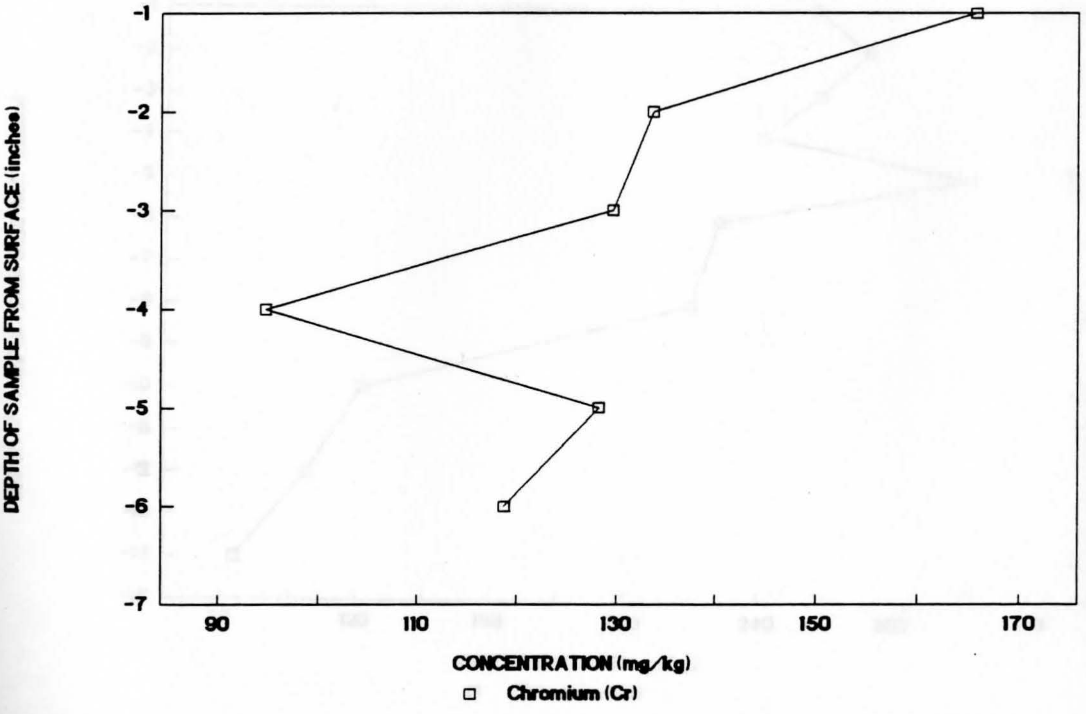


FIGURE 4.27: Chromium Concentrations (mg/kg) Varying With Depth (inches) at the Youngstown Coring Location (center channel, a half mile downstream from the Youngstown municipal discharge)

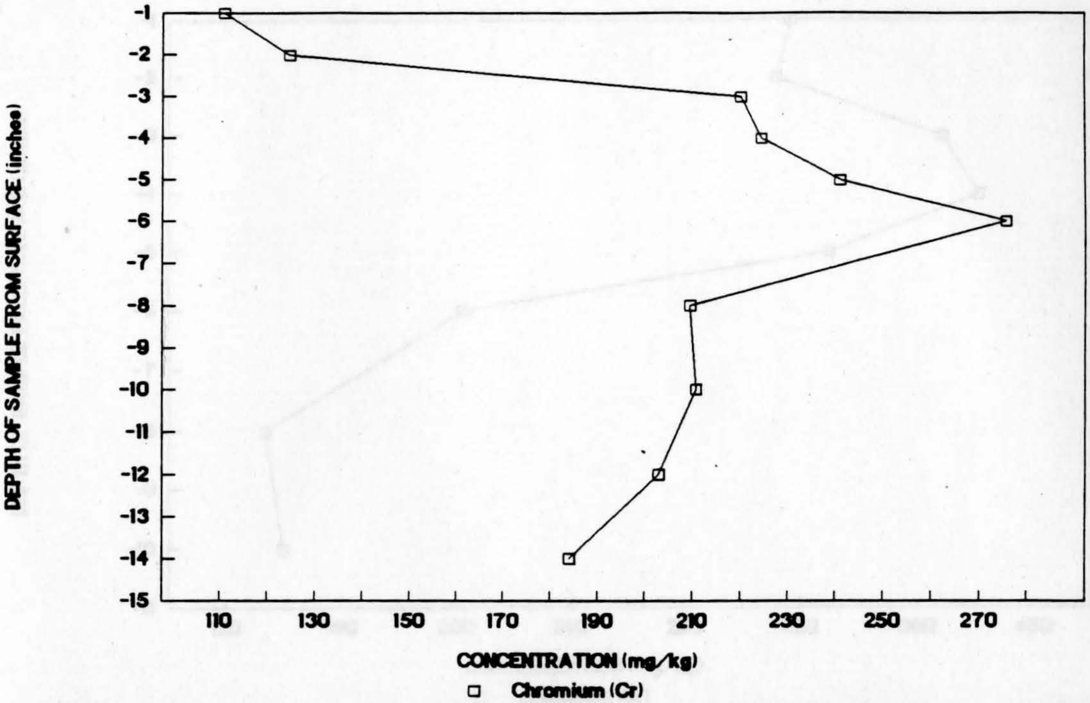


FIGURE 4.28: Chromium Concentrations (mg/kg) Varying With Depth (inches) at the Struthers Coring Location (left bank, directly across from the Struthers municipal discharge culvert)

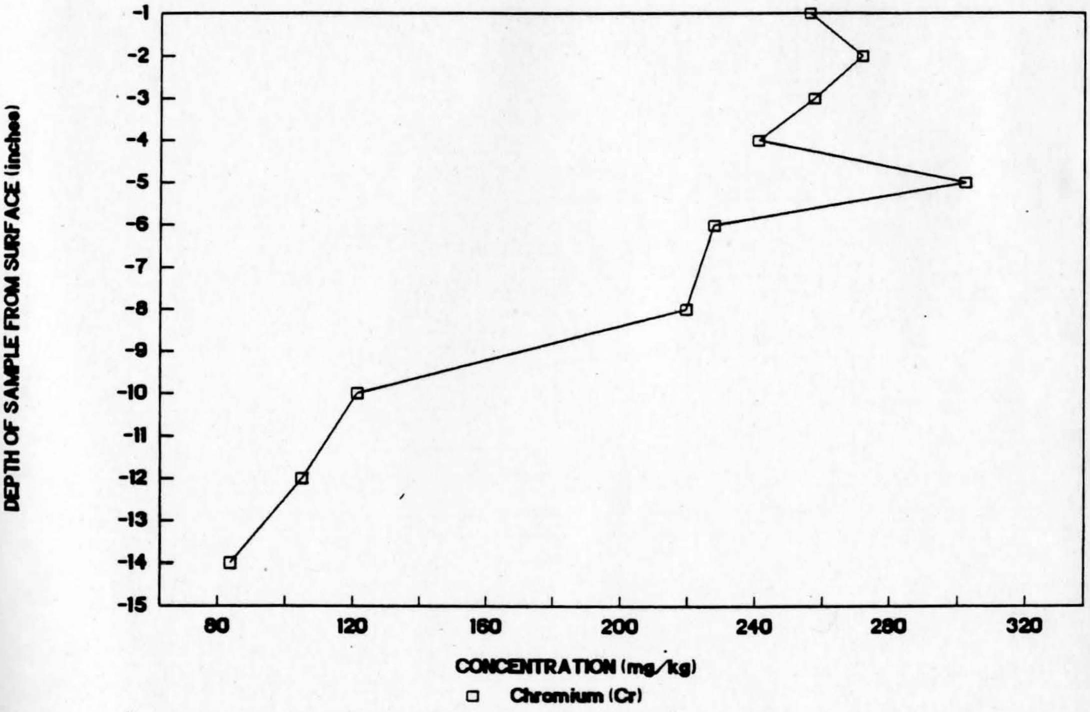


FIGURE 4.29: Chromium Concentrations (mg/kg) Varying With Depth (inches) at the Struthers Coring Location (right bank, 200 ft downstream from the Struthers municipal discharge culvert)

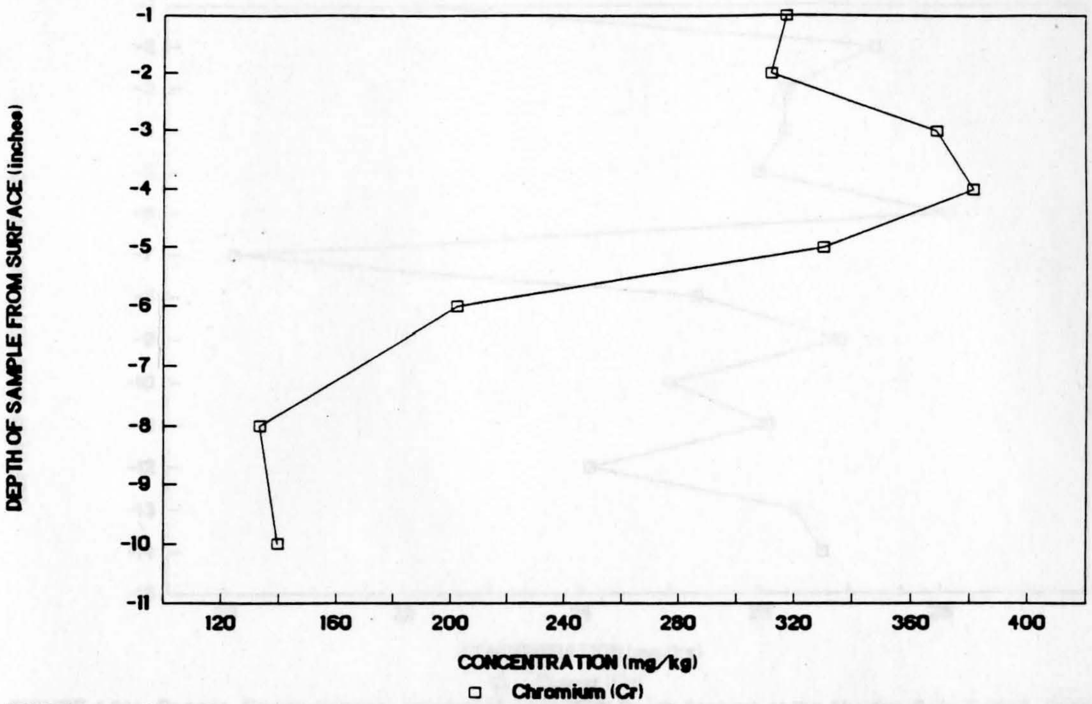


FIGURE 4.30: Chromium Concentrations (mg/kg) Varying With Depth (inches) at the Struthers Coring Location (left bank, a quarter mile downstream from the Struthers municipal discharge culvert)

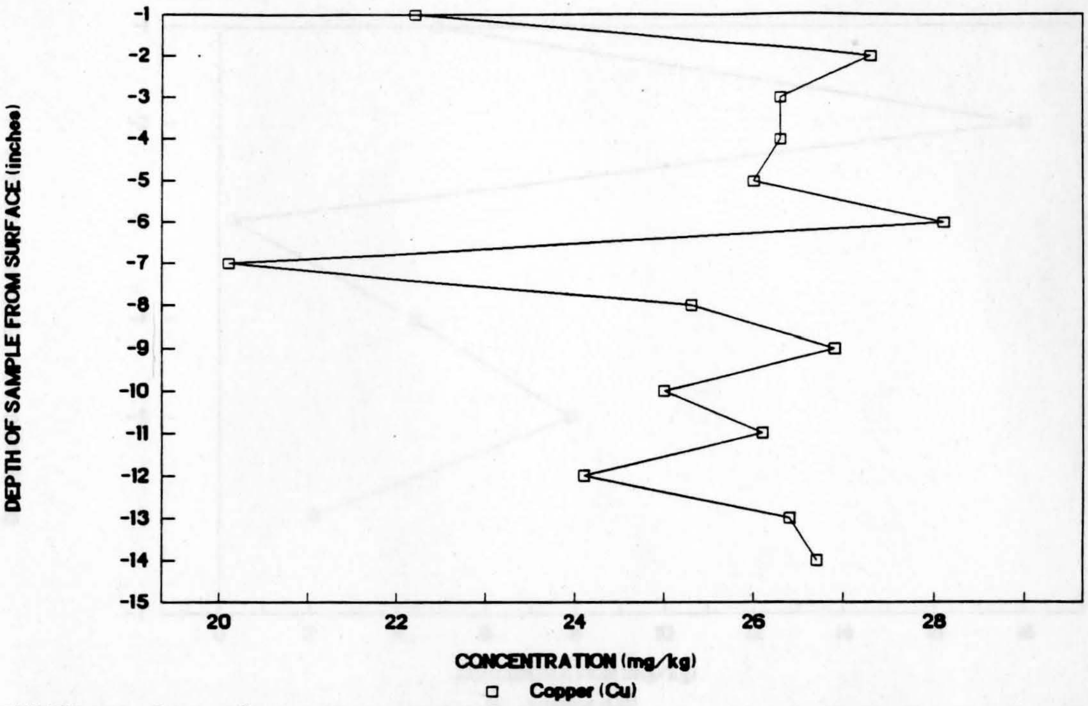


FIGURE 4.31: Copper Concentrations (mg/kg) Varying With Depth (inches) at the Newton Falls Coring Location (left bank, in vicinity of the Newton Falls water intake line)

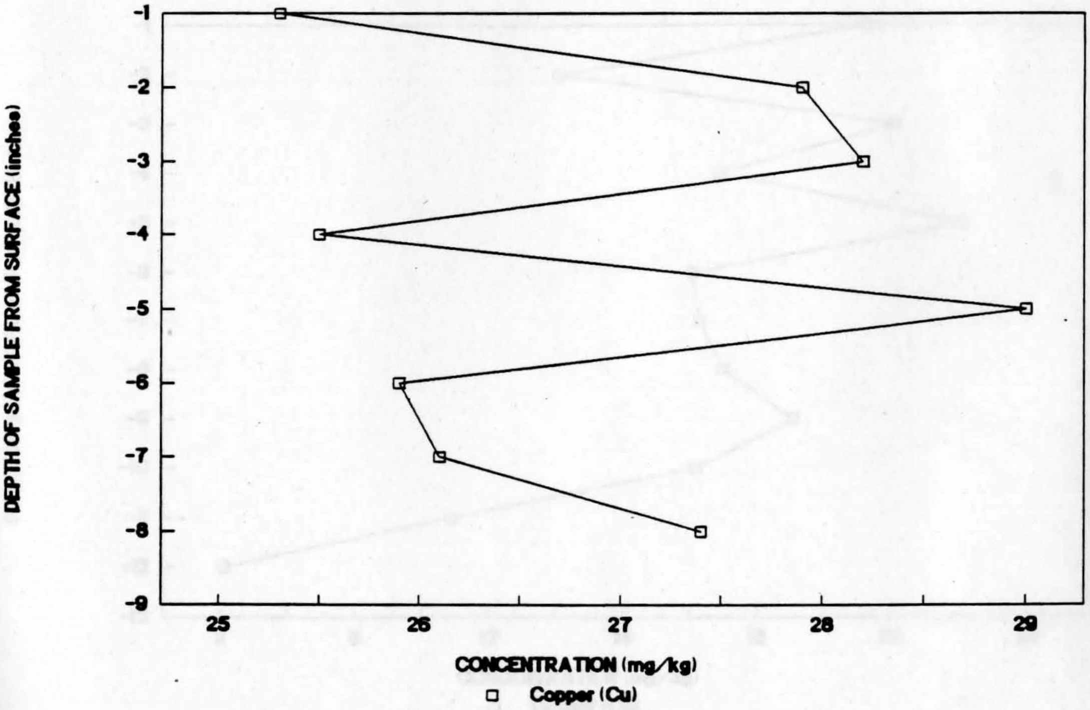


FIGURE 4.32: Copper Concentrations (mg/kg) Varying With Depth (inches) at the Newton Falls Coring Location (left channel, in vicinity of the Newton Falls water intake line)

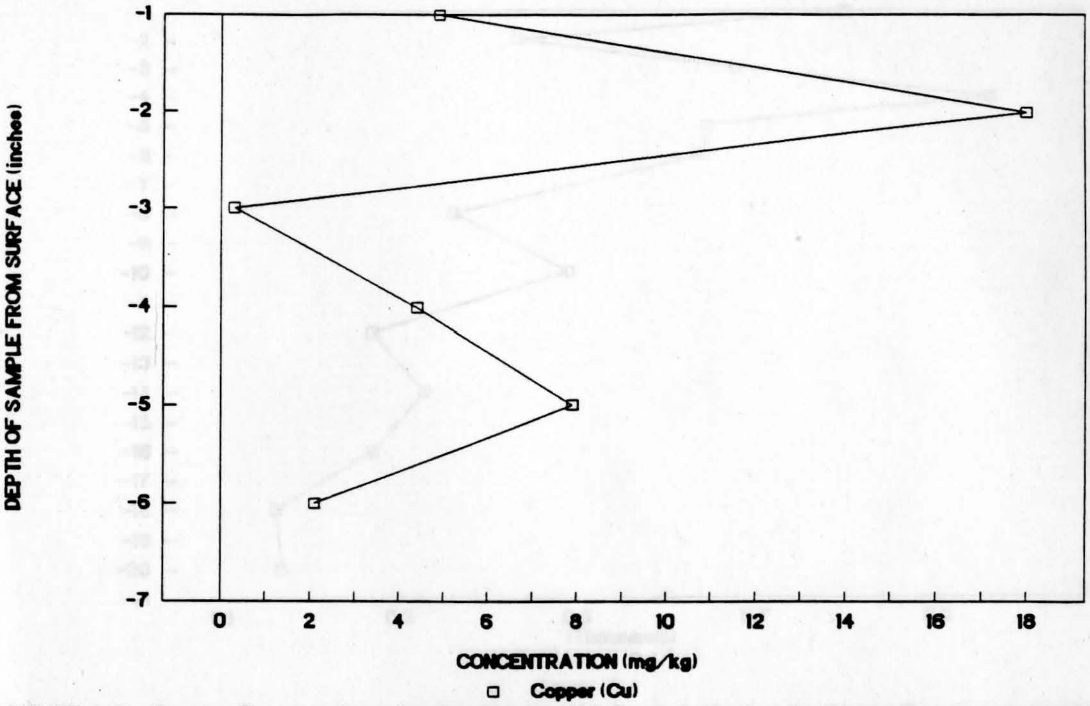


FIGURE 4.33: Copper Concentrations (mg/kg) Varying With Depth (inches) at the Newton Falls Coring Location (right channel, in vicinity of the Newton Falls water intake line)

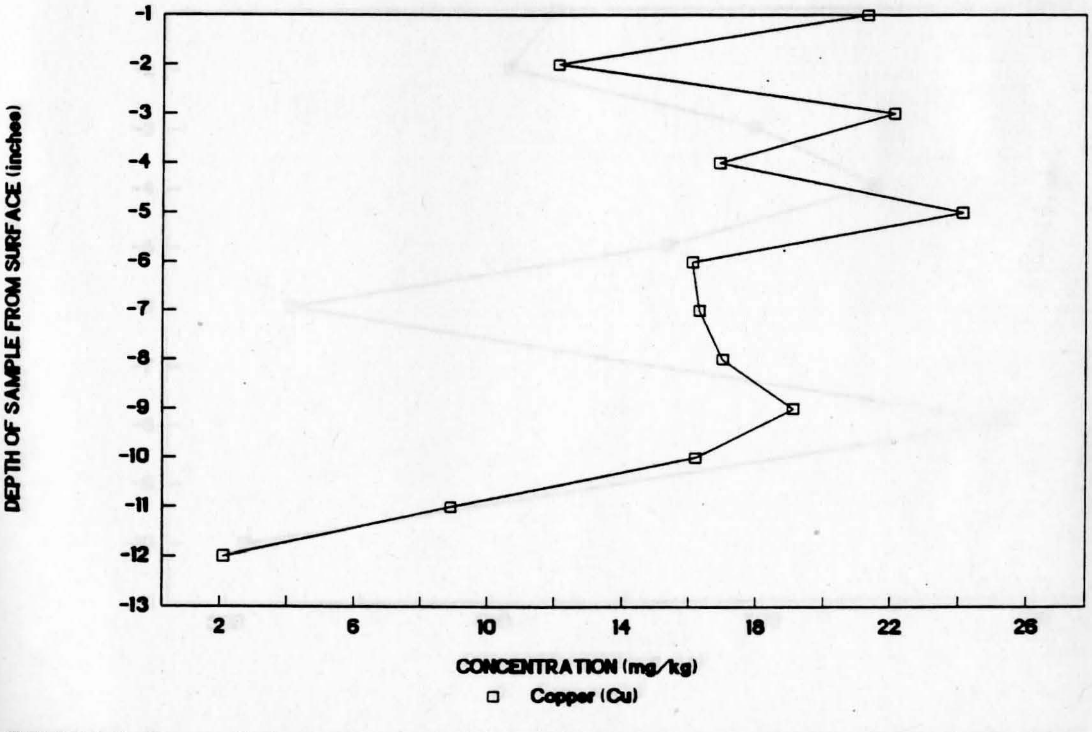


FIGURE 4.34: Copper Concentrations (mg/kg) Varying With Depth (inches) at the Newton Falls Coring Location (right bank, in vicinity of the Newton Falls water intake line)

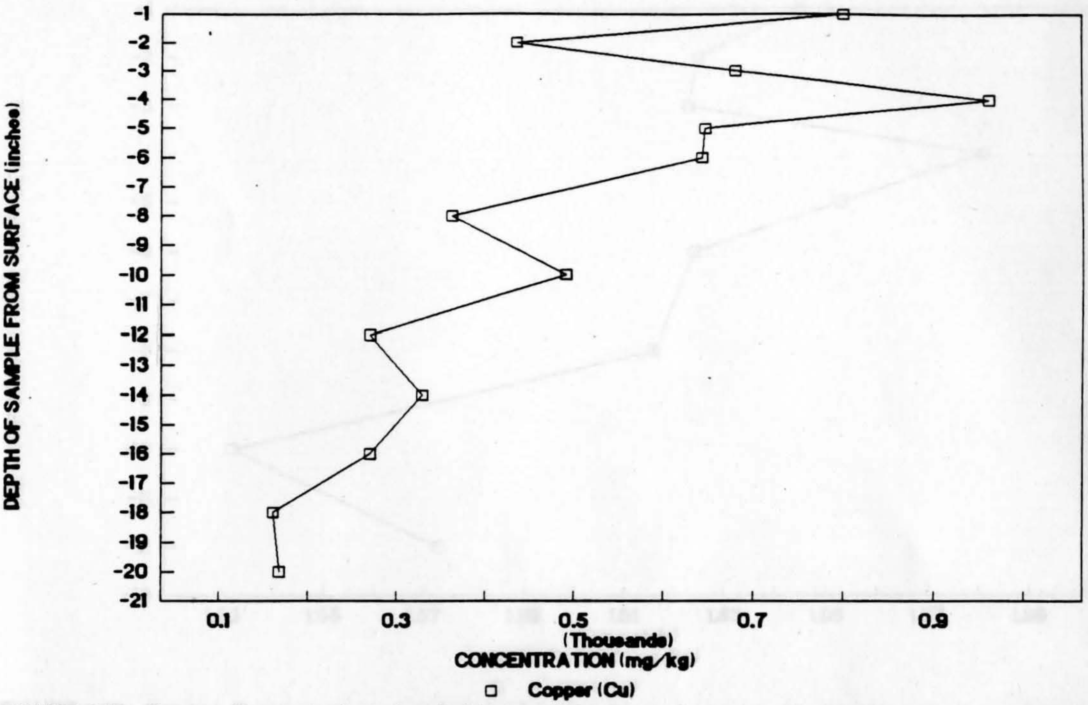


FIGURE 4.35: Copper Concentrations (mg/kg) Varying With Depth (inches) at the Warren Coring Location (left bank, directly downstream from the Copperweld discharge)

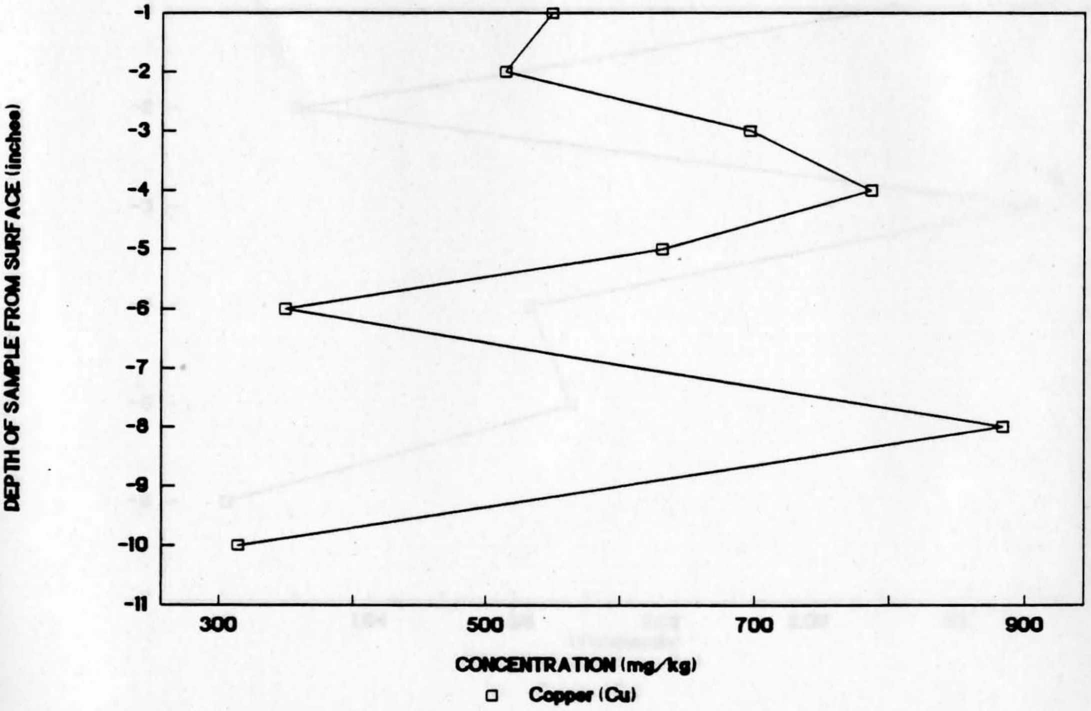


FIGURE 4.36: Copper Concentrations (mg/kg) Varying With Depth (inches) at the Warren Coring Location (right channel, directly downstream from the Copperweld discharge)

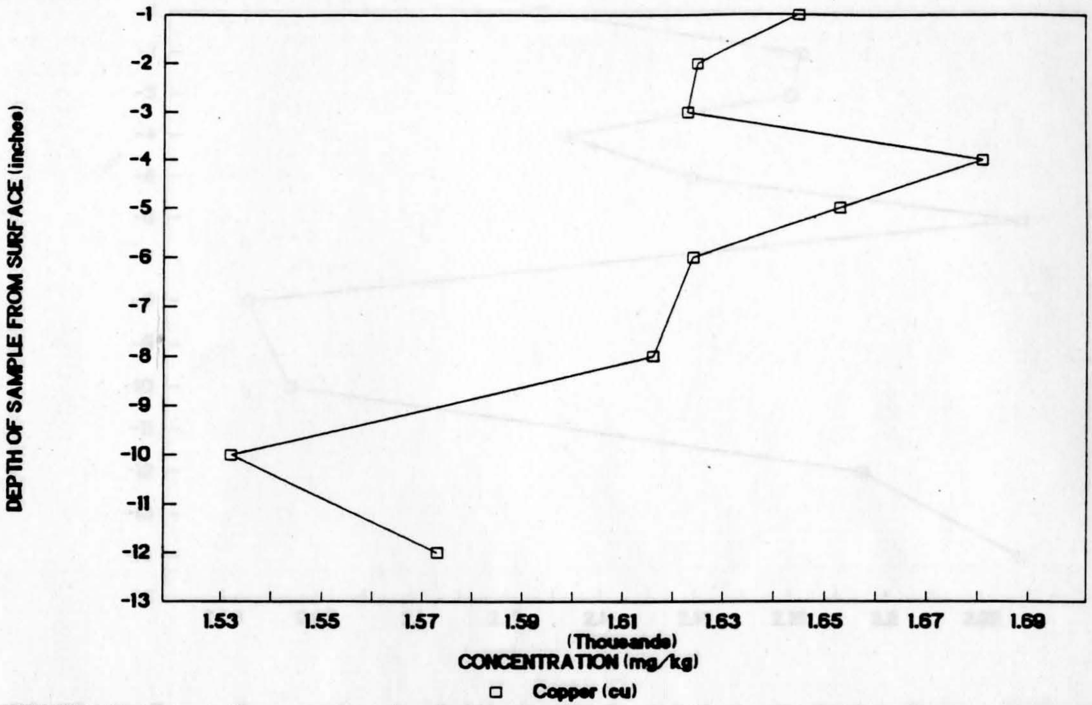


FIGURE 4.37: Copper Concentrations (mg/kg) Varying With Depth (inches) at the Youngstown Coring Location (left bank, 200 ft downstream from the Youngstown municipal discharge line)

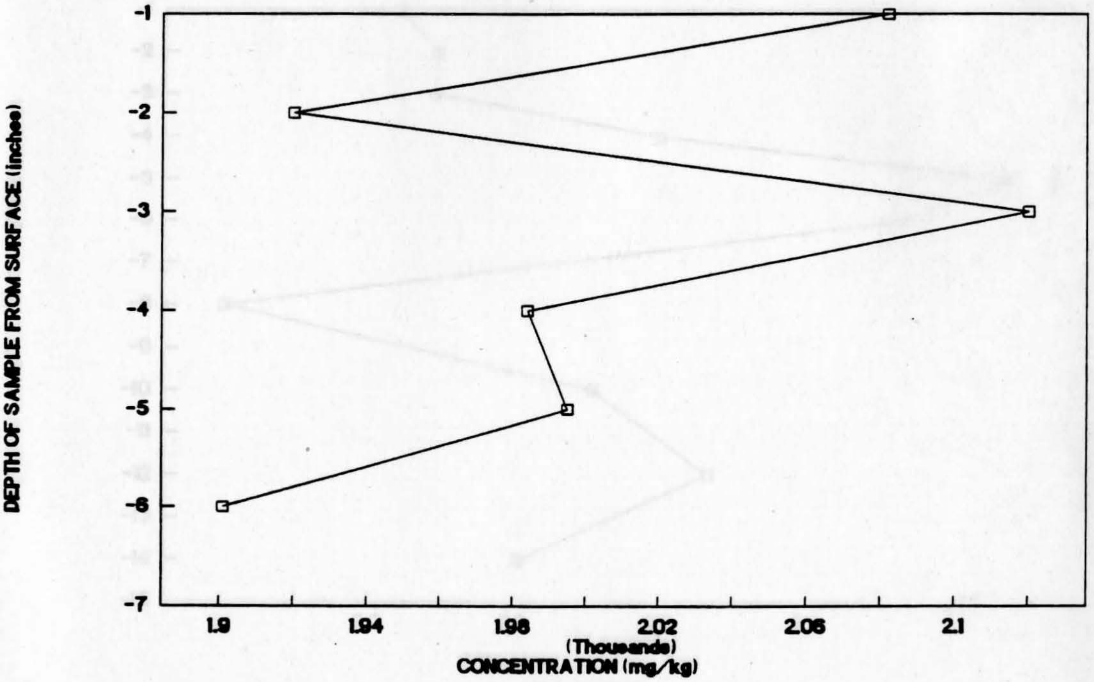


FIGURE 4.38: Copper Concentrations (mg/kg) Varying With Depth (inches) at the Youngstown Coring Location (center channel, a half mile downstream from the Youngstown municipal discharge)

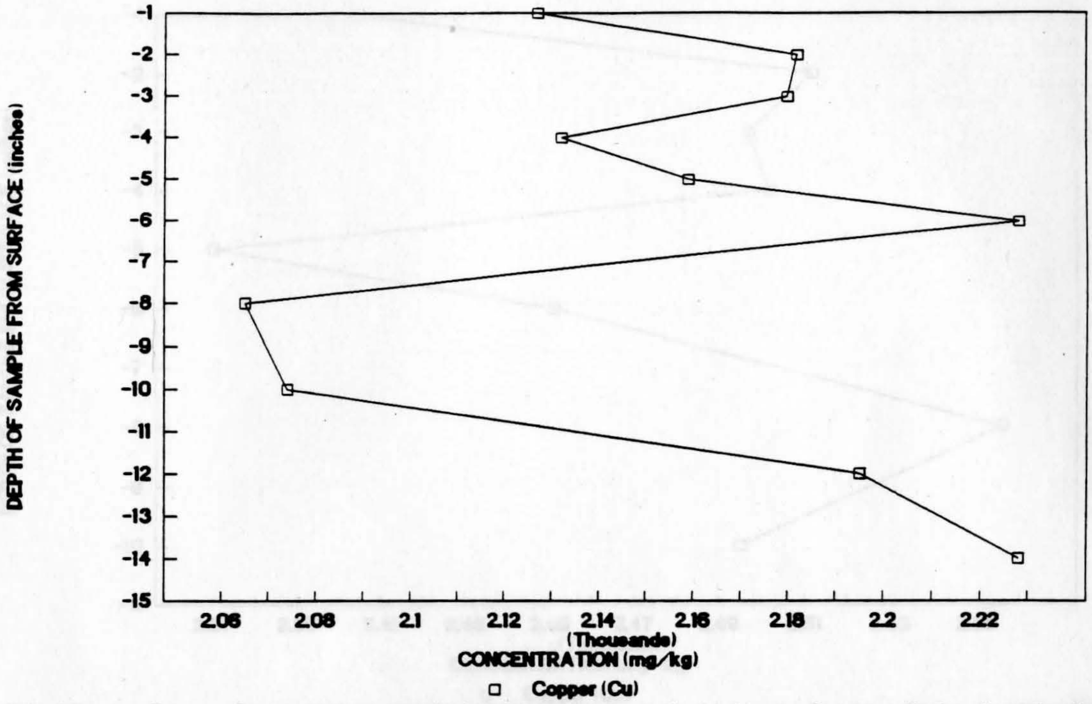


FIGURE 4.39: Copper Concentrations (mg/kg) Varying With Depth (inches) at the Struthers Coring Location (left bank, directly across from the Struthers municipal discharge culvert)

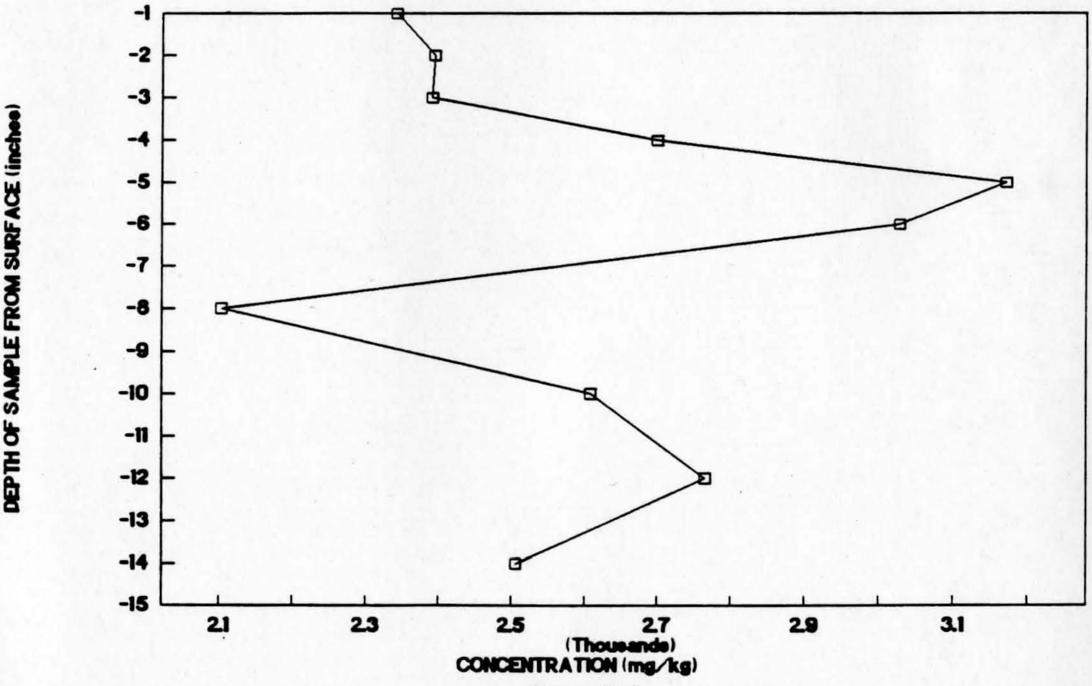


FIGURE 4.40: Copper Concentrations (mg/kg) Varying With Depth (inches) at the Struthers Coring Location (right bank, 200 ft downstream from the Struthers municipal discharge culvert)

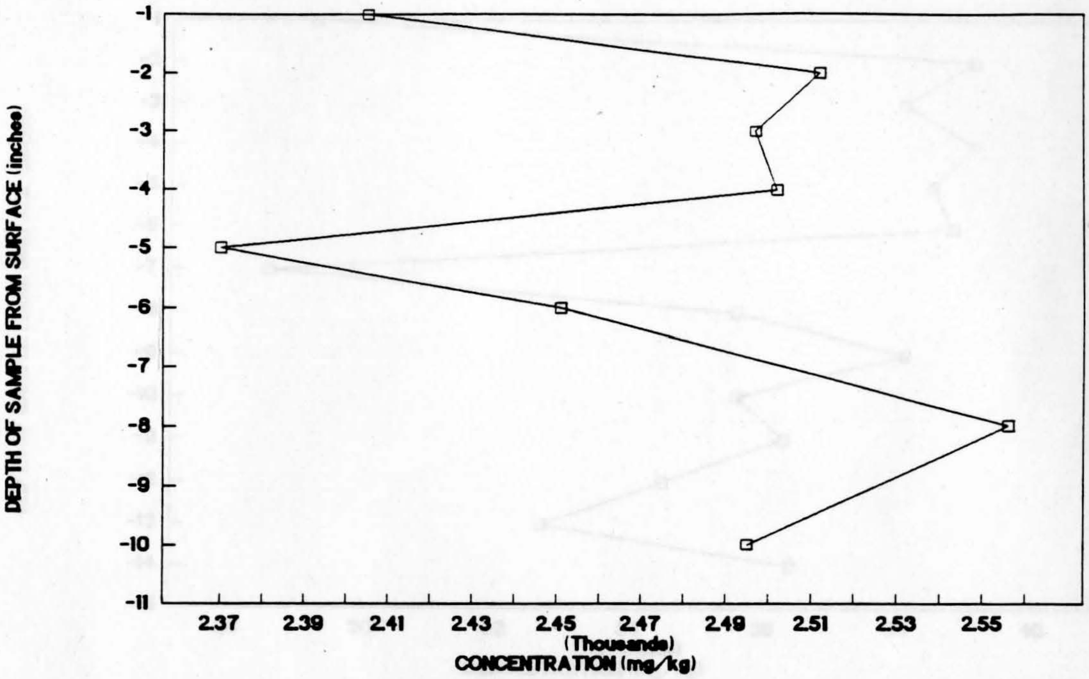


FIGURE 4.41: Copper Concentrations (mg/kg) Varying With Depth (inches) at the Struthers Coring Location (left bank, a quarter mile downstream from the Struthers municipal discharge culvert)

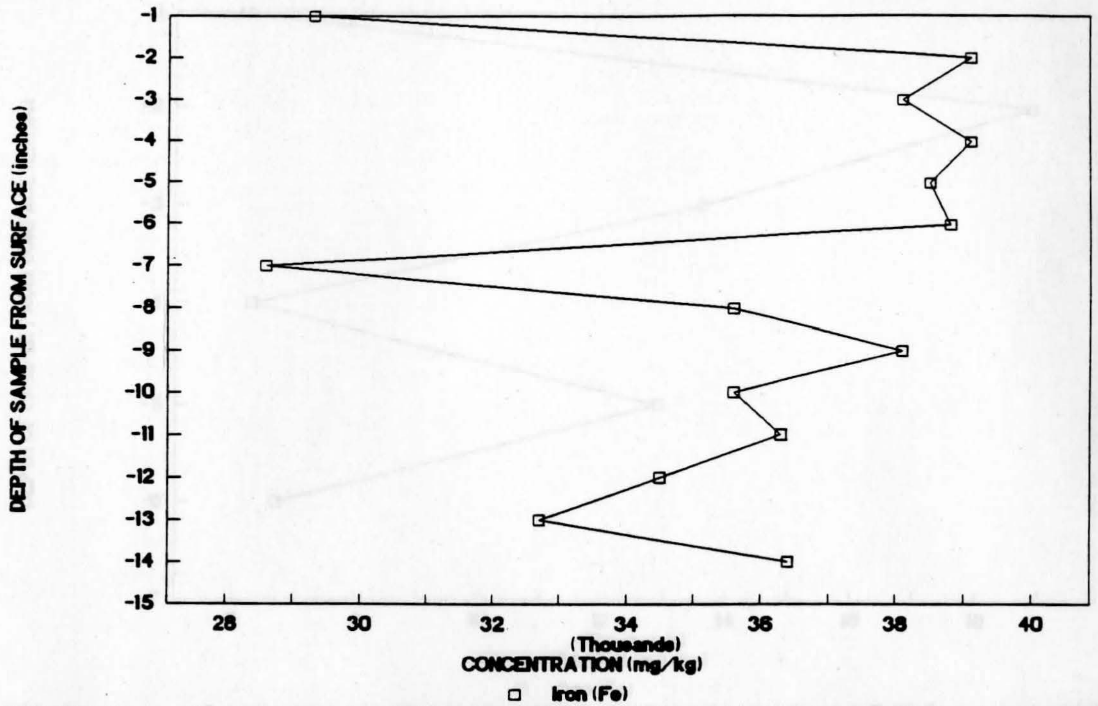


FIGURE 4.42: Iron Concentrations (mg/kg) Varying With Depth (inches) at the Newton Falls Coring Location (left bank, in vicinity of the Newton Falls water intake line)

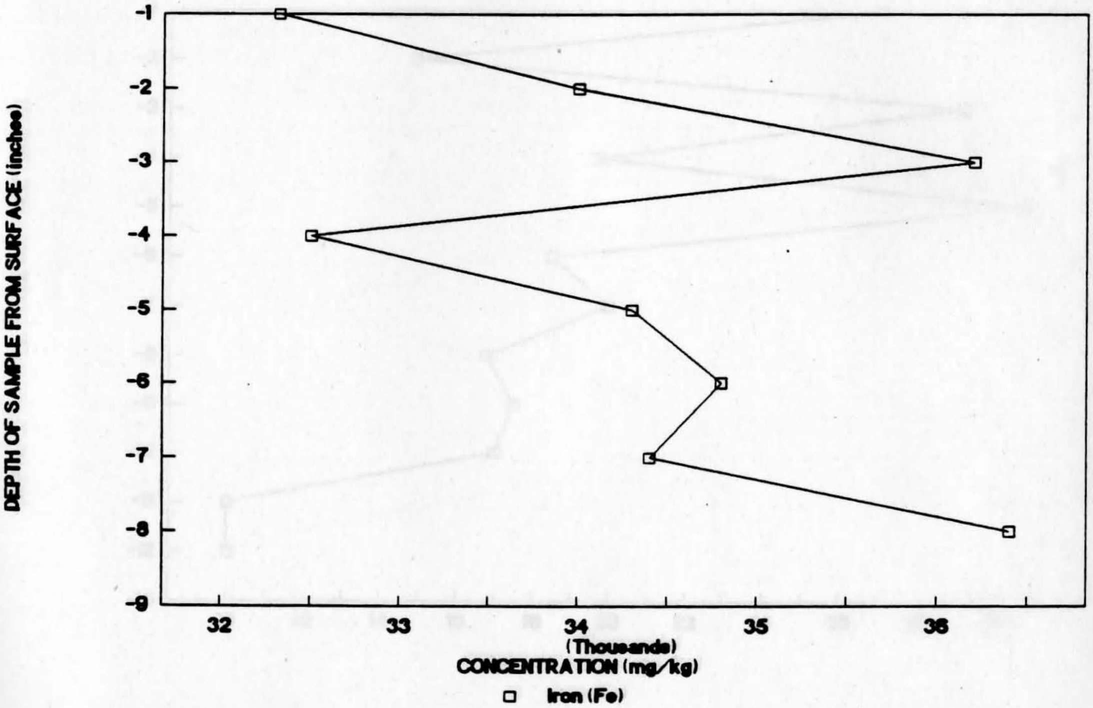


FIGURE 4.43: Iron Concentrations (mg/kg) Varying With Depth (inches) at the Newton Falls Coring Location (left channel, in vicinity of the Newton Falls water intake line)

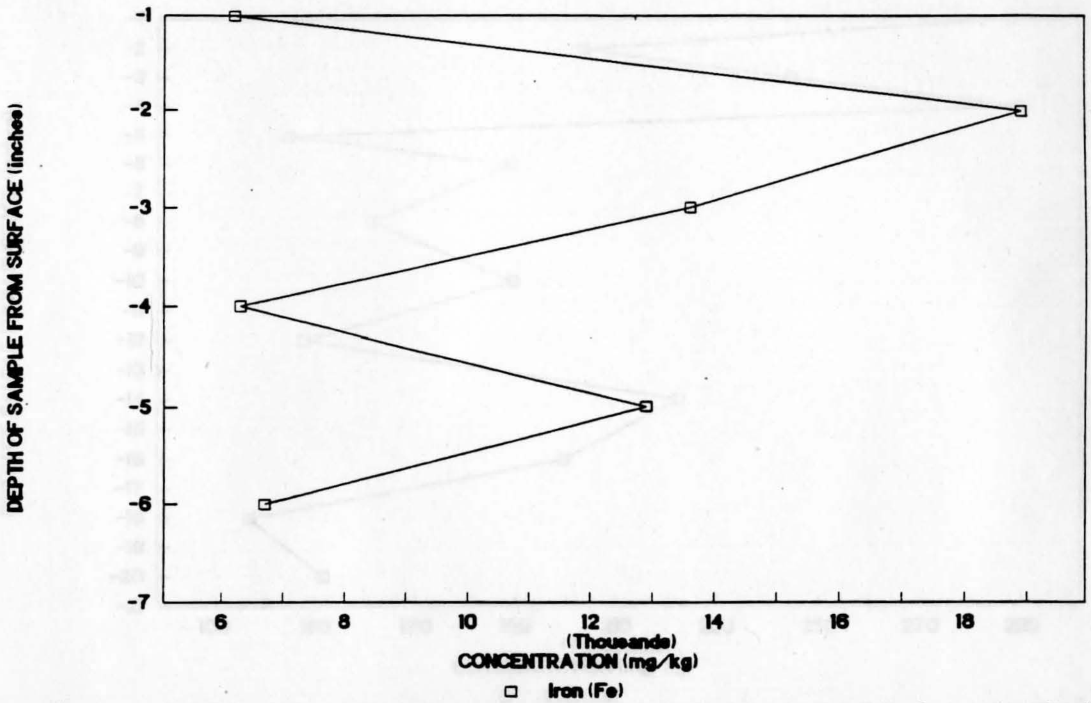


FIGURE 4.44: Iron Concentrations (mg/kg) Varying With Depth (inches) at the Newton Falls Coring Location (right channel, in vicinity of the Newton Falls water intake line)

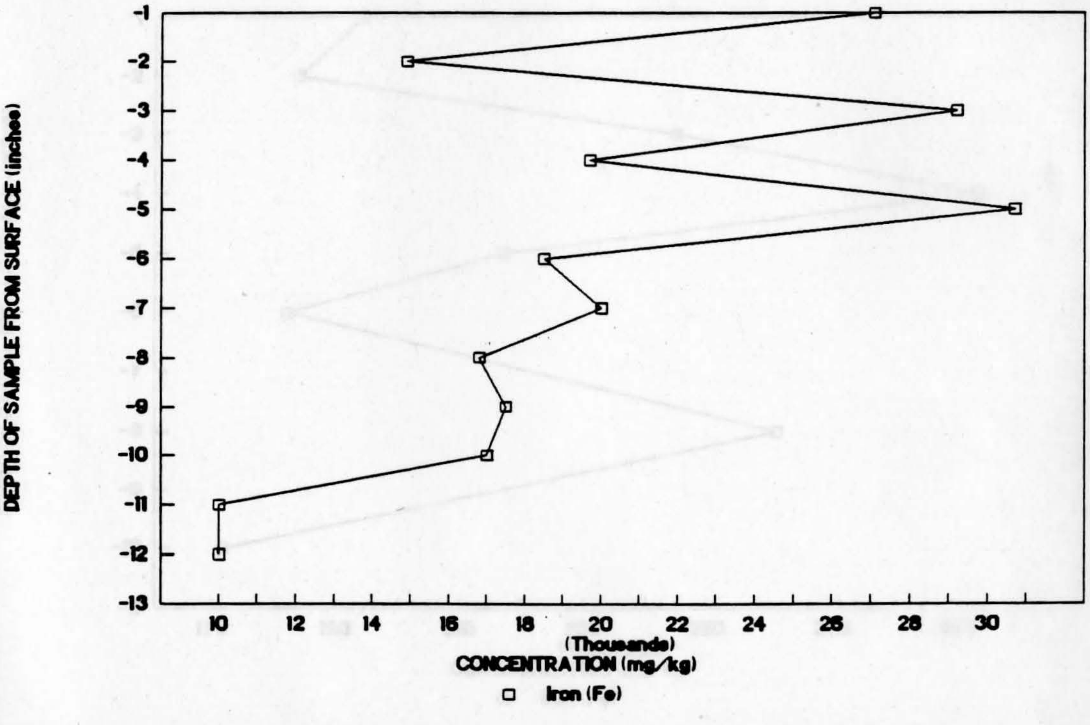


FIGURE 4.45: Iron Concentrations (mg/kg) Varying With Depth (inches) at the Newton Falls Coring Location (right bank, in vicinity of the Newton Falls water intake line)

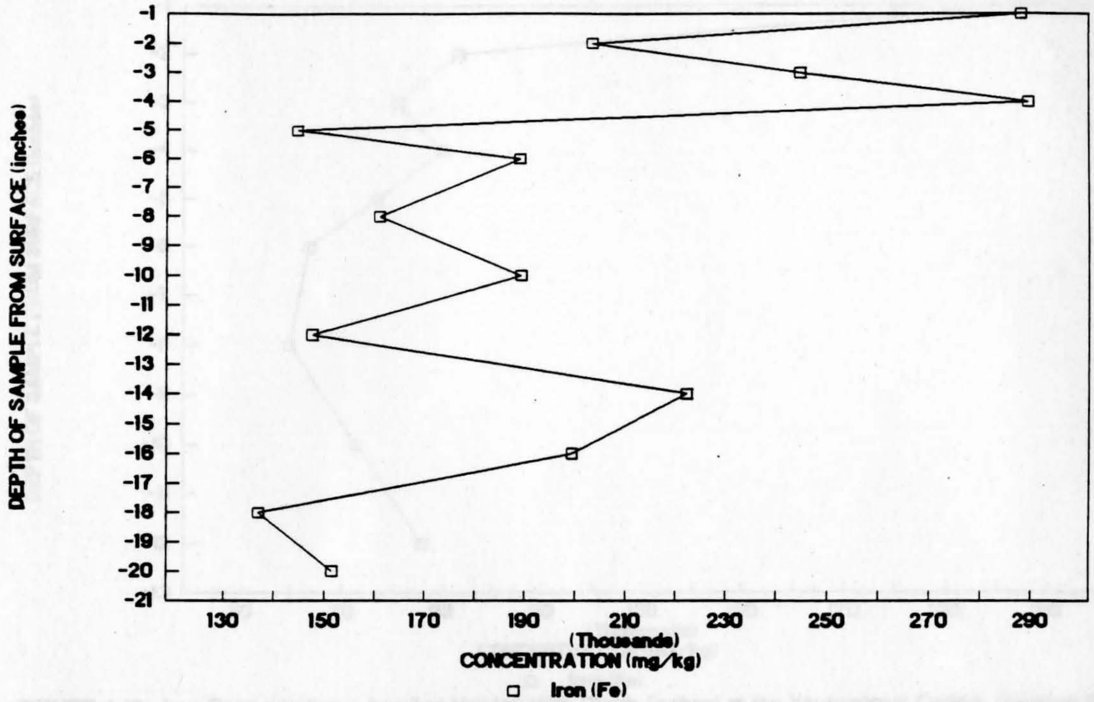


FIGURE 4.46: Iron Concentrations (mg/kg) Varying With Depth (inches) at the Warren Coring Location (left bank, directly downstream from the Copperweld discharge)

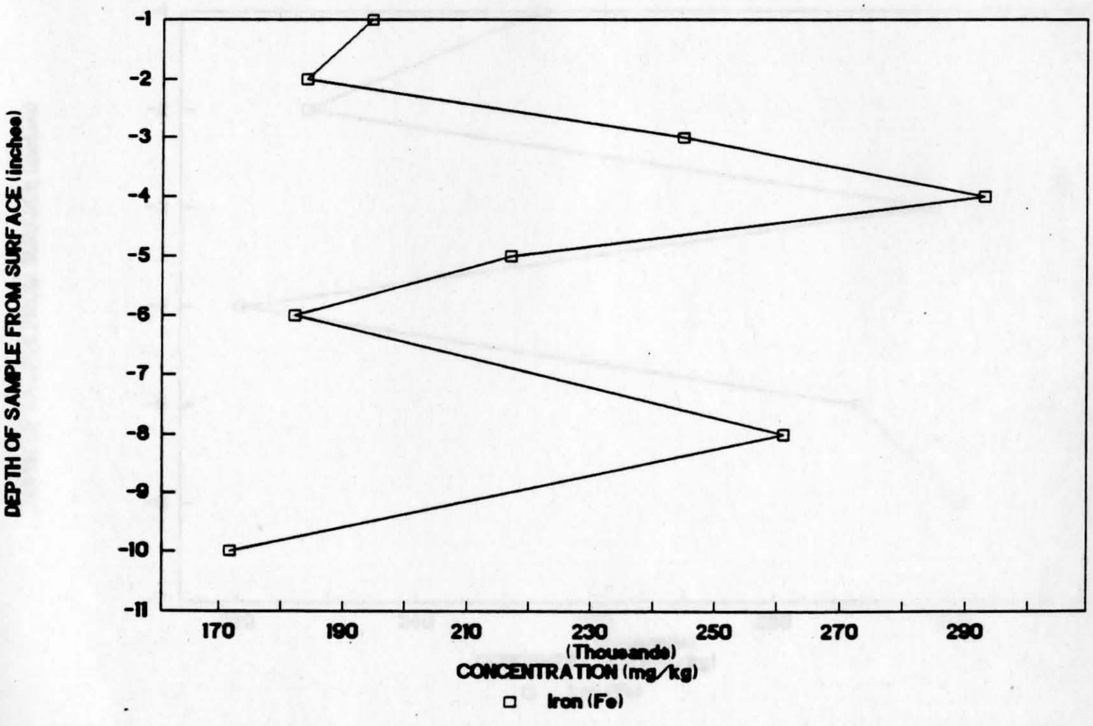


FIGURE 4.47: Iron Concentrations (mg/kg) Varying With Depth (inches) at the Warren Coring Location (right channel, directly downstream from the Copperweld discharge)

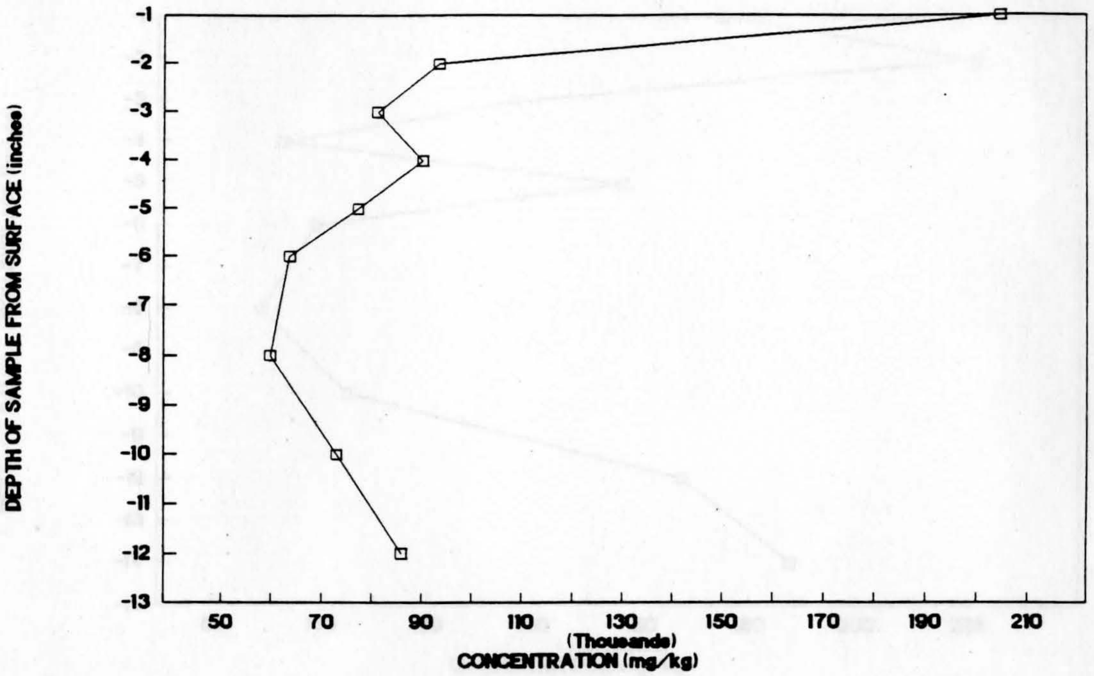


FIGURE 4.48: Iron Concentrations (mg/kg) Varying With Depth (inches) at the Youngstown Coring Location (left bank, 200 ft downstream from the Youngstown municipal discharge line)

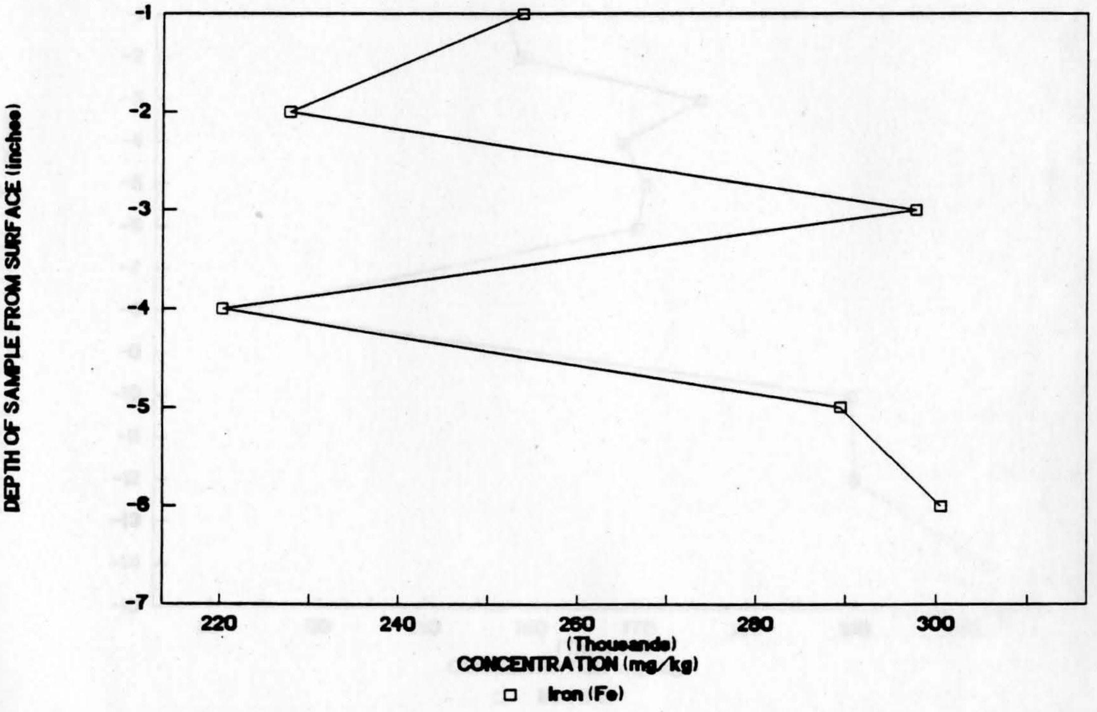


FIGURE 4.49: Iron Concentrations (mg/kg) Varying With Depth (inches) at the Youngstown Coring Location (center channel, a half mile downstream from the Youngstowns municipal discharge)

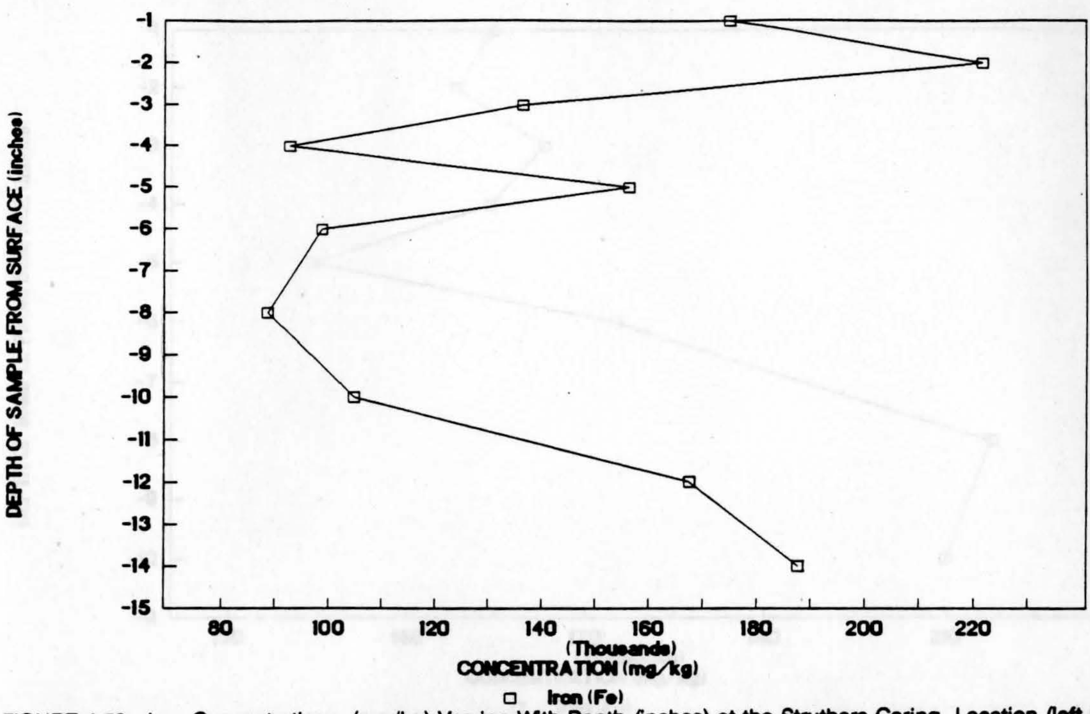


FIGURE 4.50: Iron Concentrations (mg/kg) Varying With Depth (inches) at the Struthers Coring Location (left bank, directly across from the Struthers municipal discharge culvert)

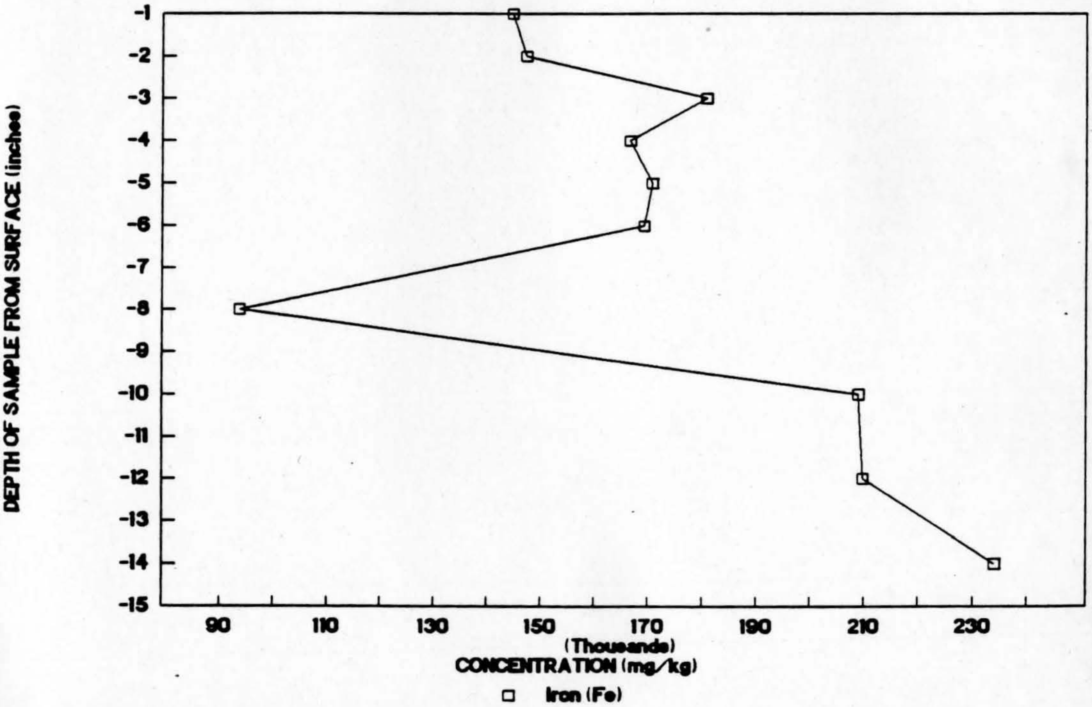


FIGURE 4.51: Iron Concentrations (mg/kg) Varying With Depth (inches) at the Struthers Coring Location (right bank, 200 ft downstream from the Struthers municipal discharge culvert)

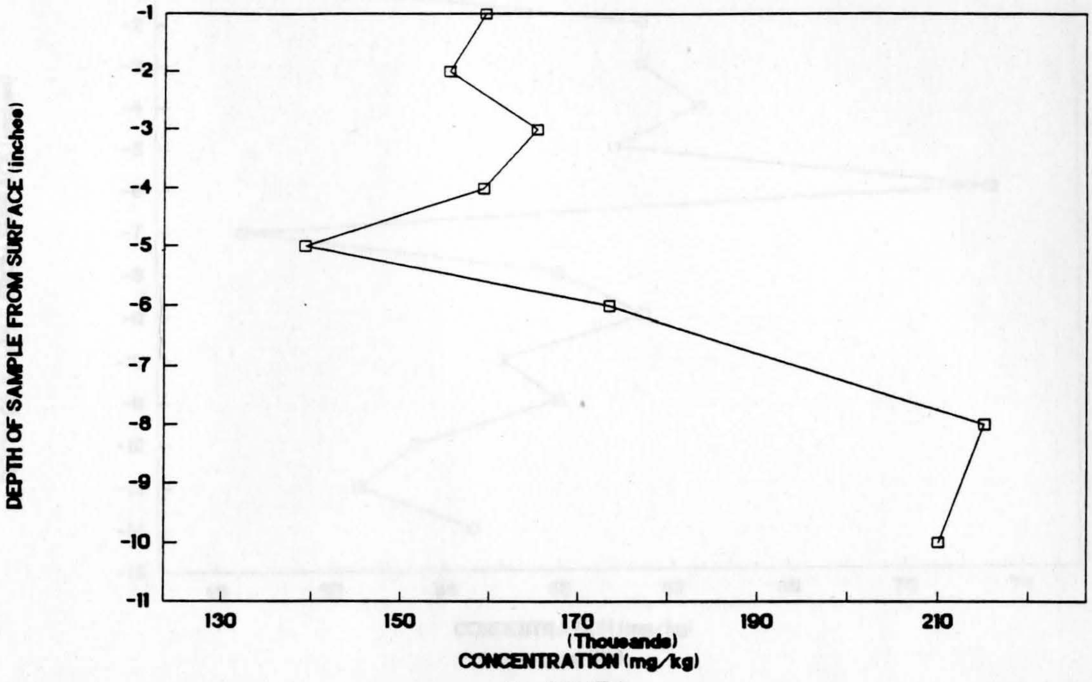


FIGURE 4.52: Iron Concentrations (mg/kg) Varying With Depth (inches) at the Struthers Coring Location (left bank, a quarter mile downstream from the Struthers municipal discharge culvert)

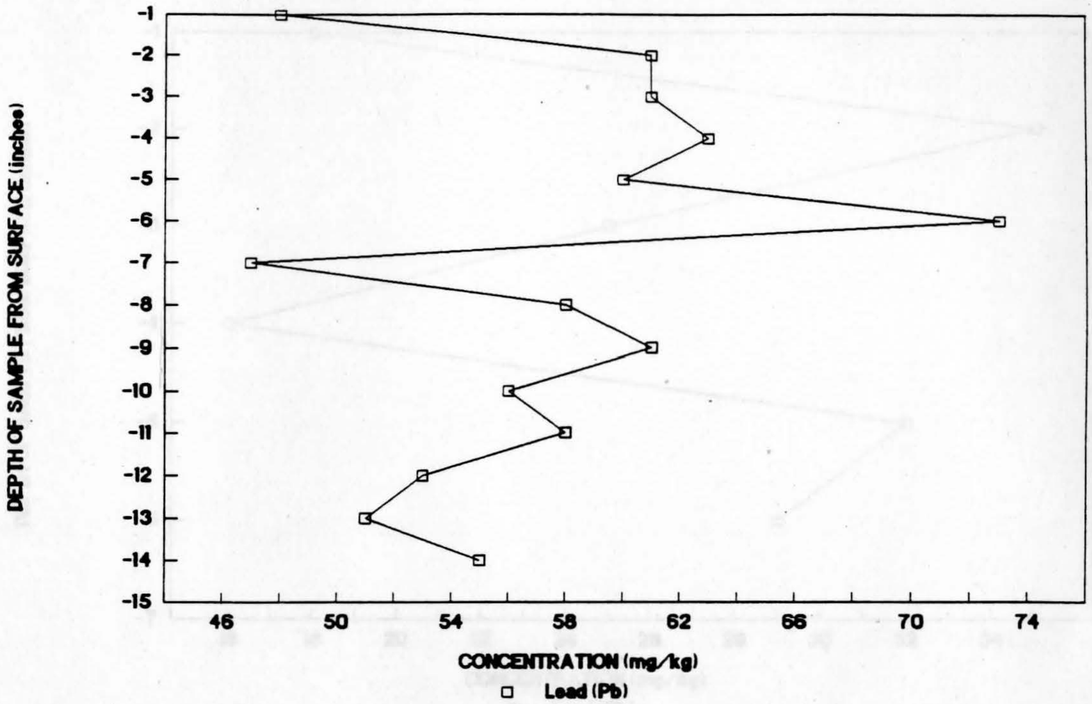


FIGURE 4.53: Lead Concentrations (mg/kg) Varying With Depth (inches) at the Newton Falls Coring Location (left bank, in vicinity of the Newton Falls water intake line)

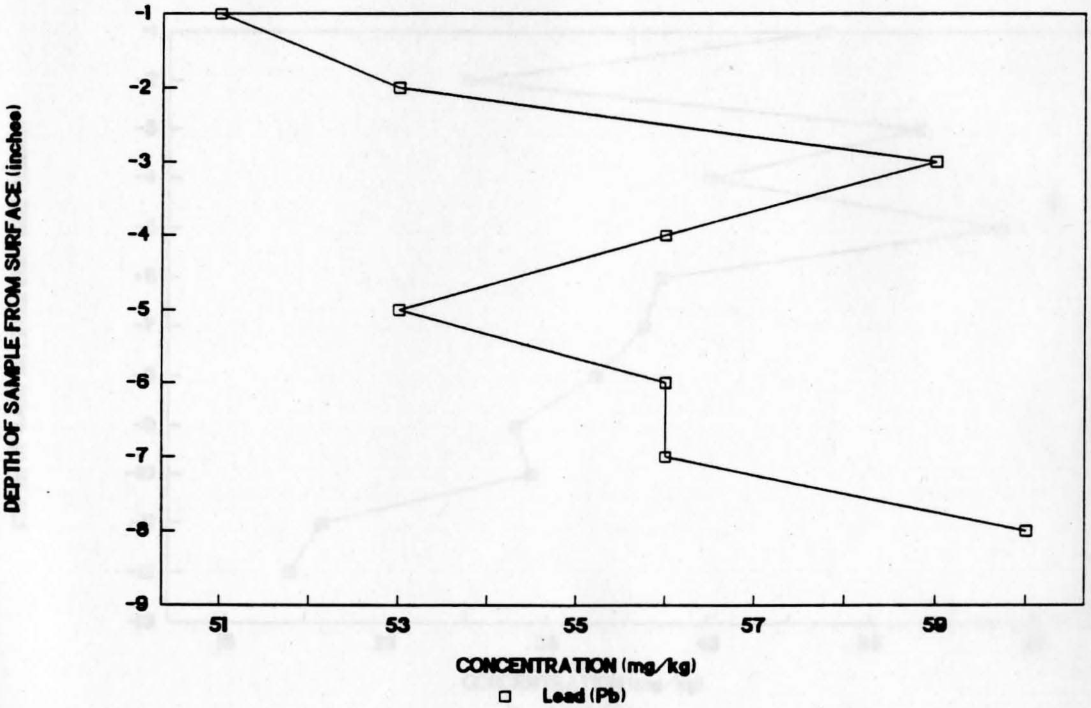


FIGURE 4.54: Lead Concentrations (mg/kg) Varying With Depth (inches) at the Newton Falls Coring Location (left channel, in vicinity of the Newton Falls water intake line)

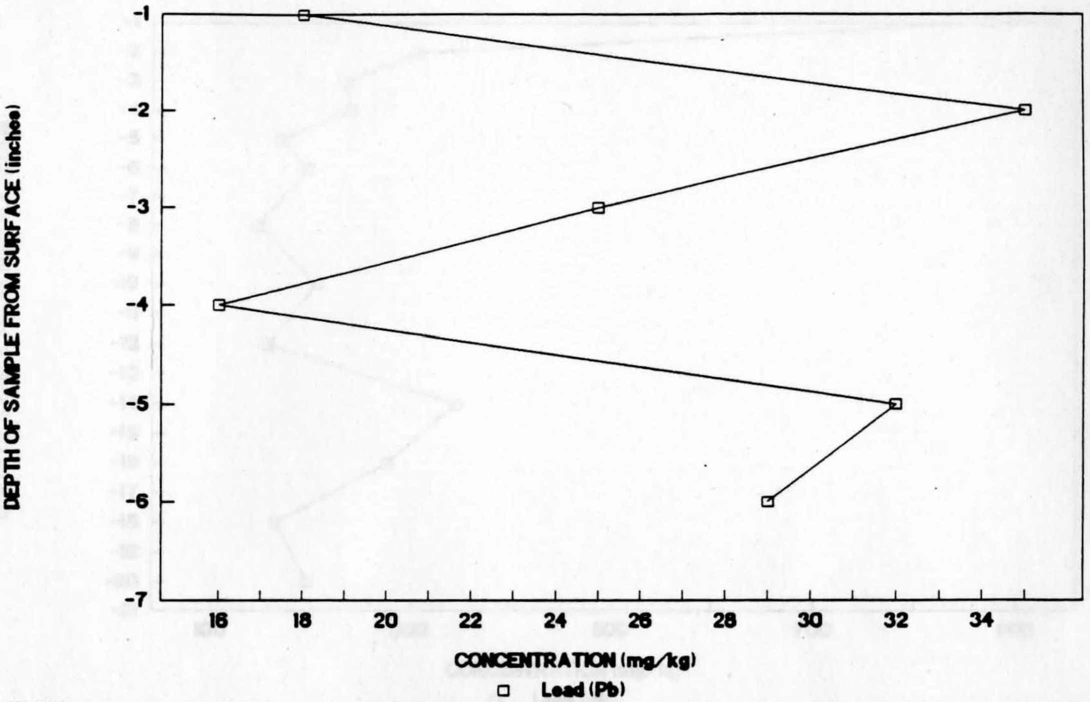


FIGURE 4.55: Lead Concentrations (mg/kg) Varying With Depth (inches) at the Newton Falls Coring Location (right channel, in vicinity of the Newton Falls water intake line)

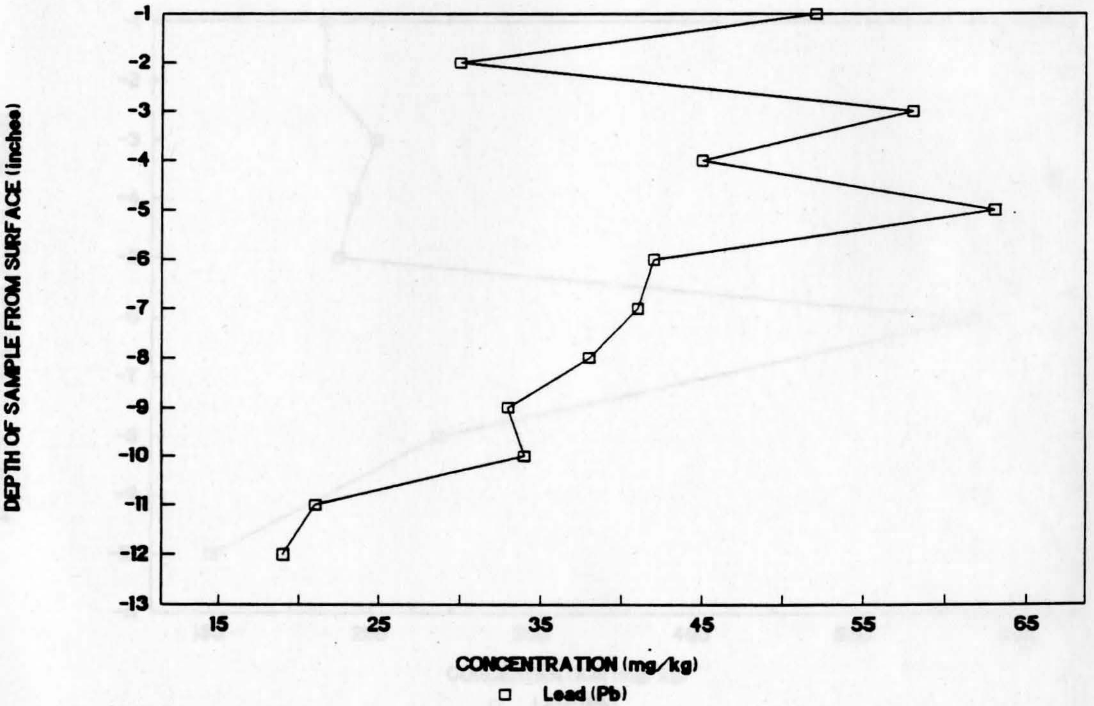


FIGURE 4.56: Lead Concentrations (mg/kg) Varying With Depth (inches) at the Newton Falls Coring Location (right bank, in vicinity of the Newton Falls water intake line)

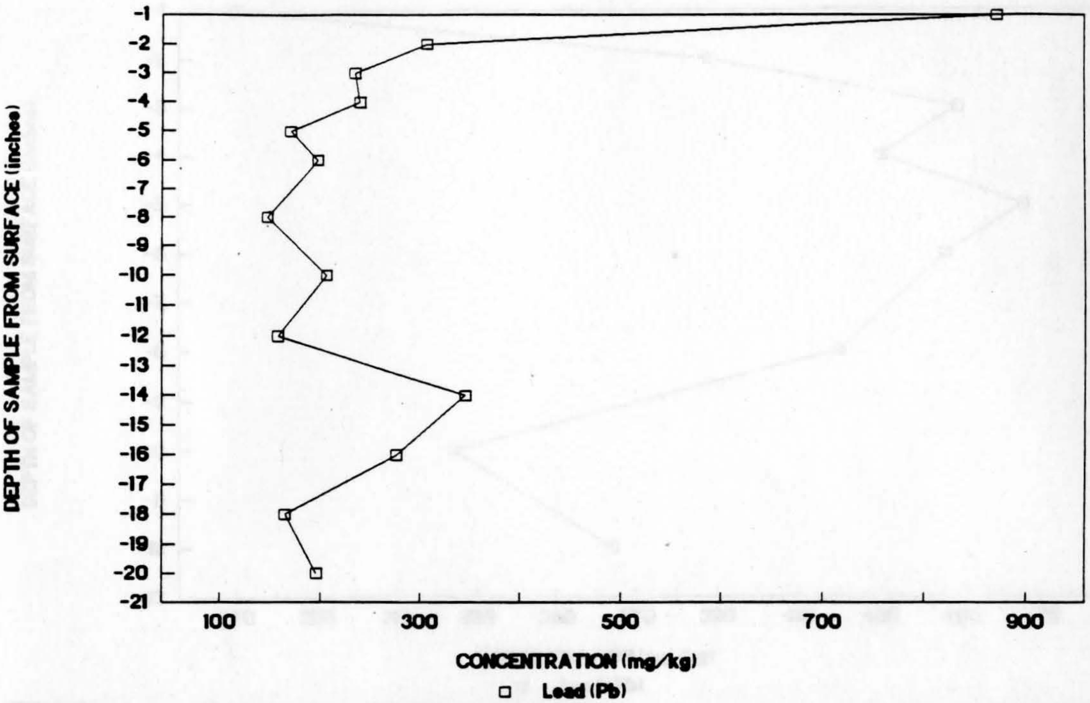


FIGURE 4.57: Lead Concentrations (mg/kg) Varying With Depth (inches) at the Warren Coring Location (left bank, directly downstream from the Copperweld discharge)

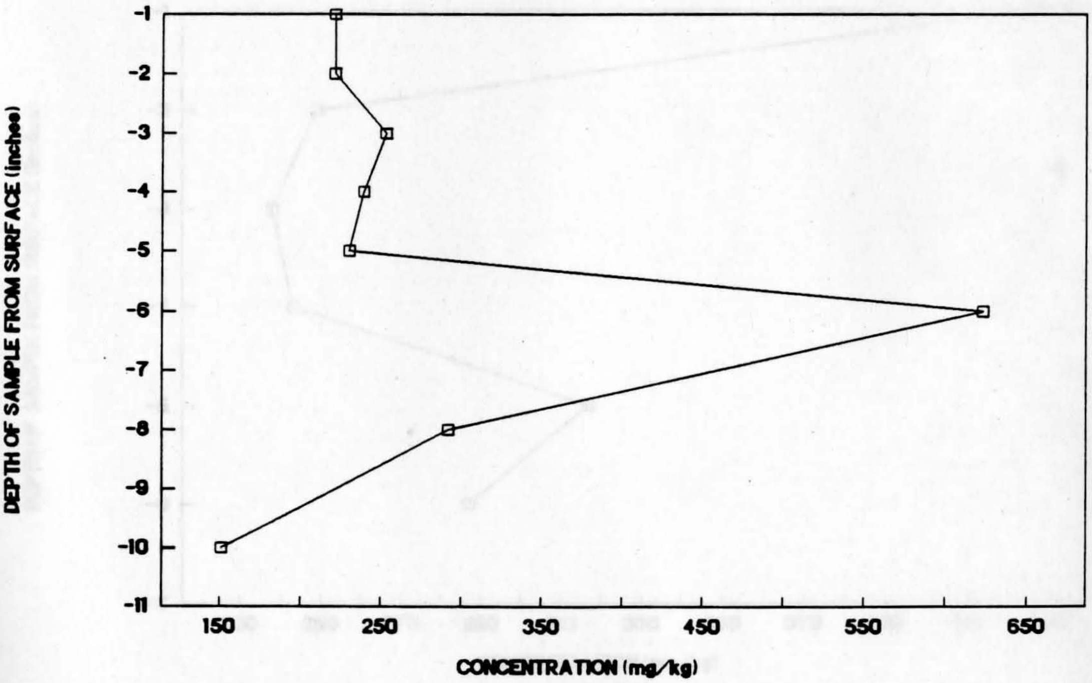


FIGURE 4.58: Lead Concentrations (mg/kg) Varying With Depth (inches) at the Warren Coring Location (right channel, directly downstream from the Copperweld discharge)

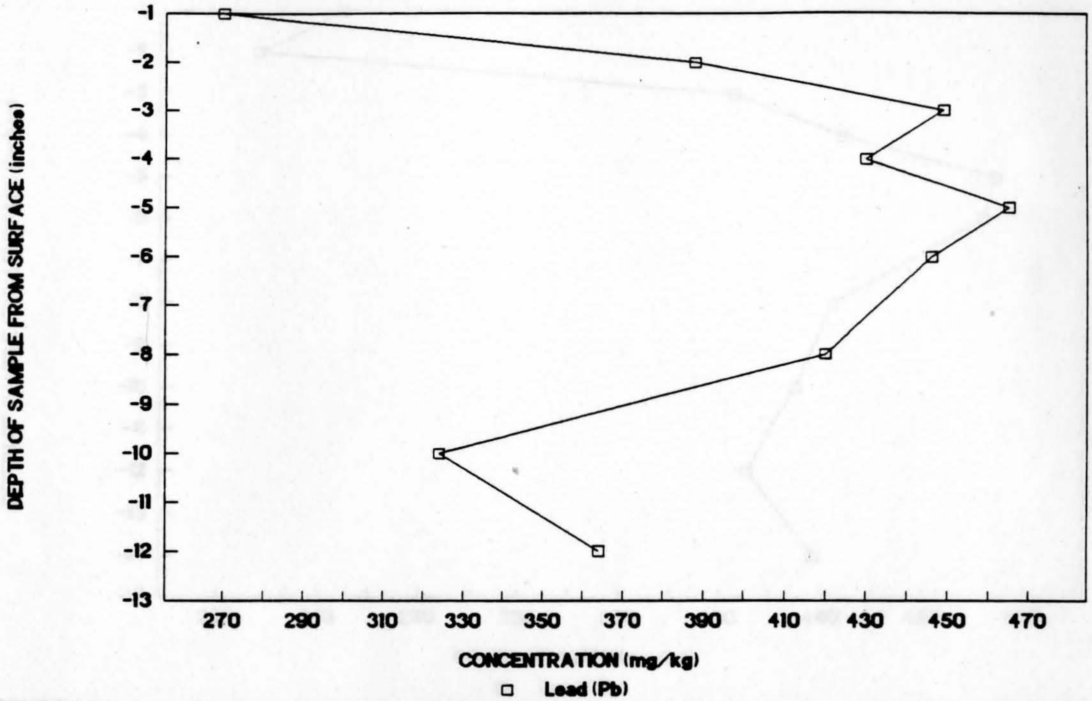


FIGURE 4.59: Lead Concentrations (mg/kg) Varying With Depth (inches) at the Youngstown Coring Location (left bank, 200 ft downstream from the Youngstown municipal discharge line)

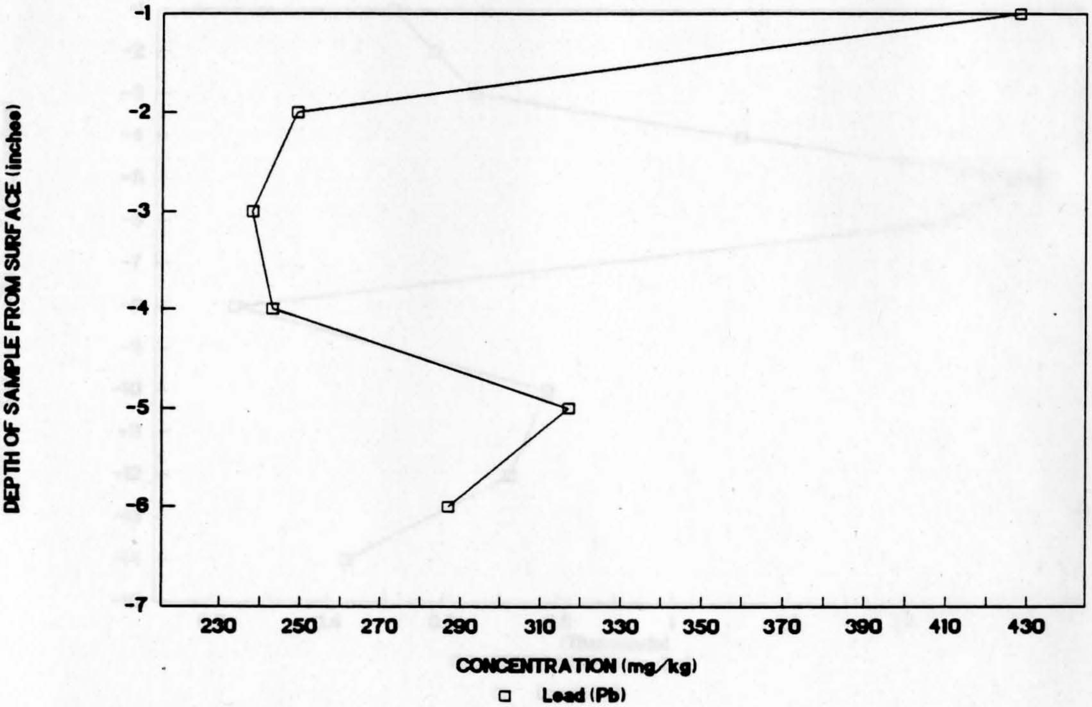


FIGURE 4.60: Lead Concentrations (mg/kg) Varying With Depth (inches) at the Youngstown Coring Location (center channel, a half mile downstream from the Youngstowns municipal discharge)

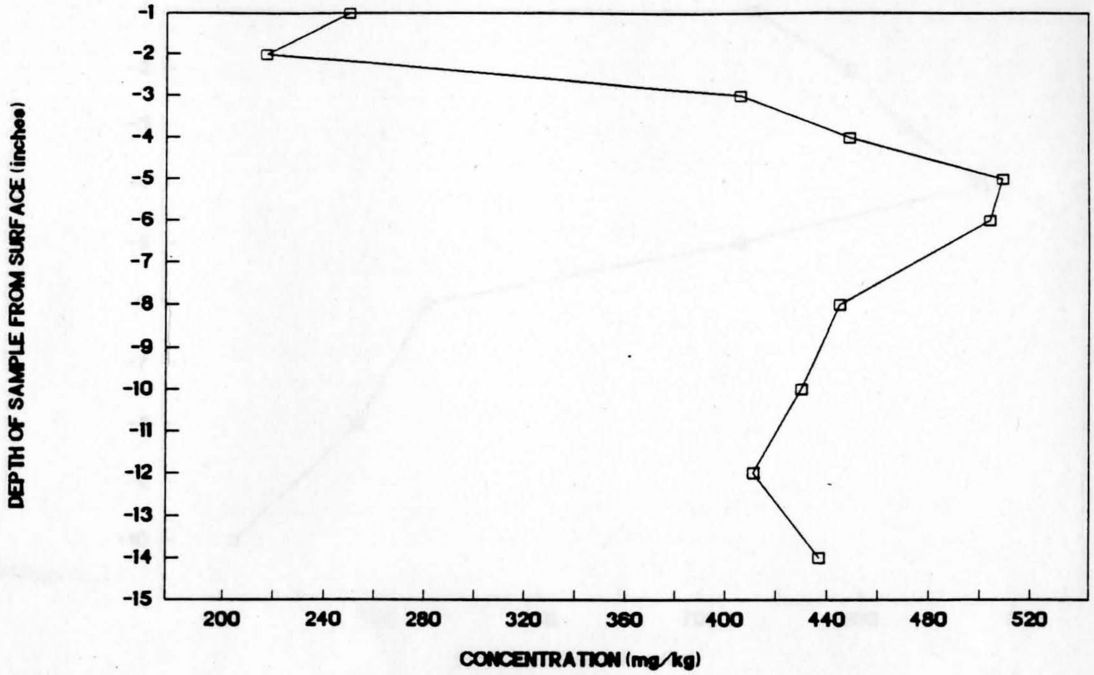


FIGURE 4.61: Lead Concentrations (mg/kg) Varying With Depth (inches) at the Struthers Coring Location (left bank, directly across from the Struthers municipal discharge culvert)

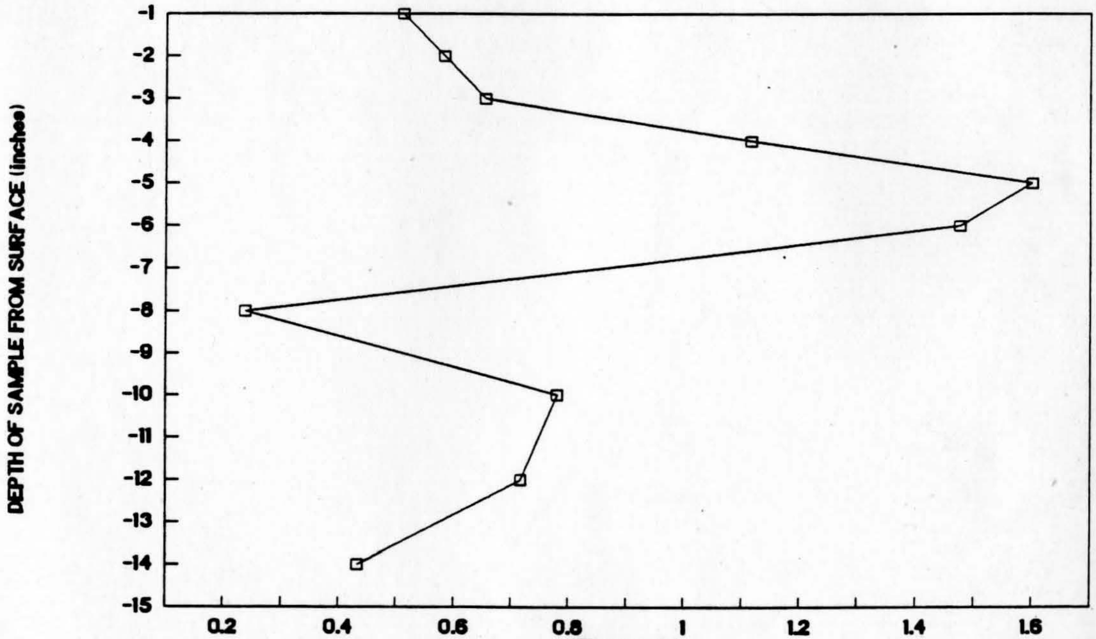


FIGURE 4.62: Lead Concentrations (mg/kg) Varying With Depth (inches) at the Struthers Coring Location (right bank, 200 ft downstream from the Struthers municipal discharge culvert)

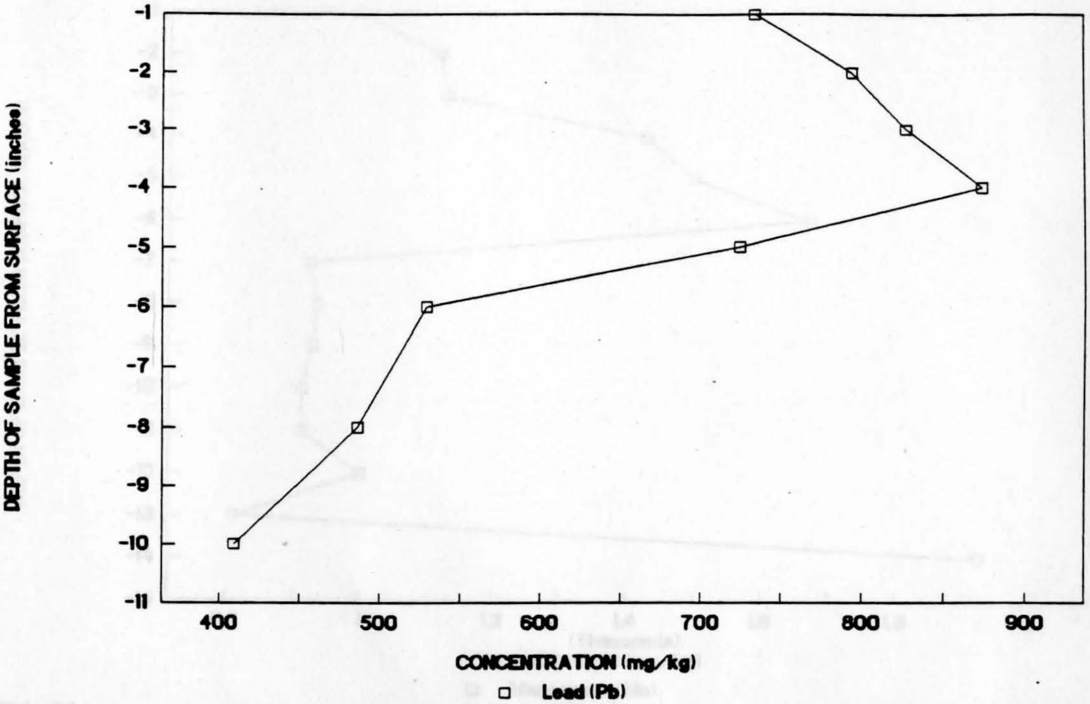


FIGURE 4.63: Lead Concentrations (mg/kg) Varying With Depth (inches) at the Struthers Coring Location (left bank, a quarter mile downstream from the Struthers municipal discharge culvert)

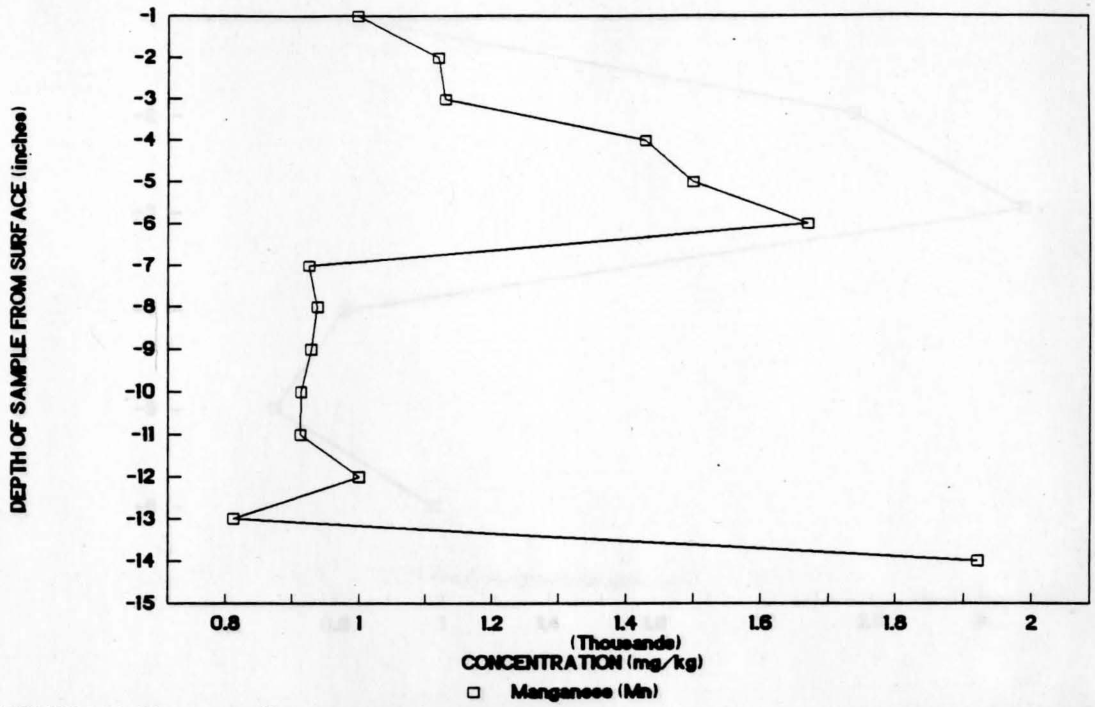


FIGURE 4.64: Manganese Concentrations (mg/kg) Varying With Depth (inches) at the Newton Falls Coring Location (left bank, in vicinity of the Newton Falls water intake line)

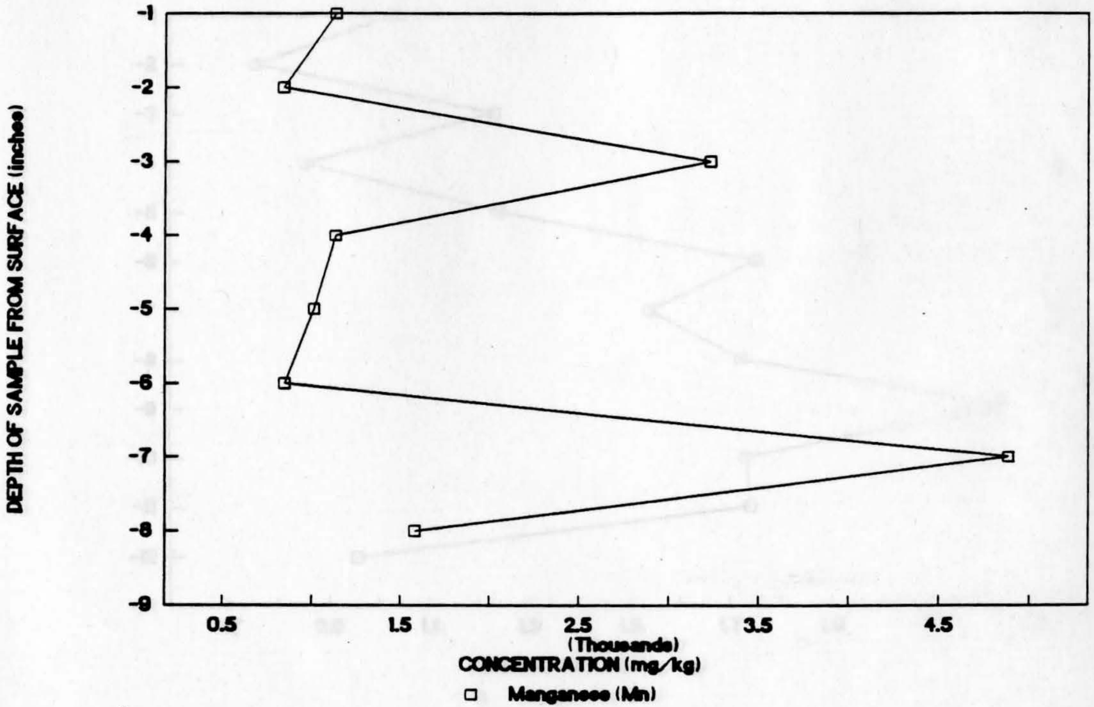


FIGURE 4.65: Manganese Concentrations (mg/kg) Varying With Depth (inches) at the Newton Falls Coring Location (left channel, in vicinity of the Newton Falls water intake line)

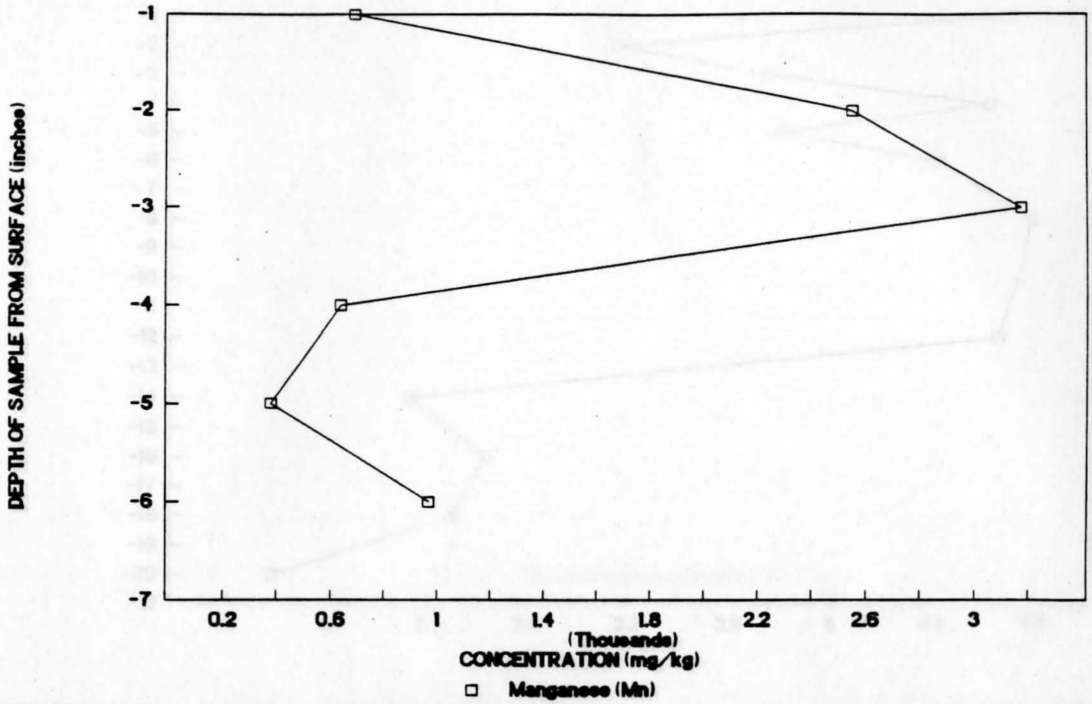


FIGURE 4.66: Manganese Concentrations (mg/kg) Varying With Depth (inches) at the Newton Falls Coring Location (right channel, in vicinity of the Newton Falls water intake line)

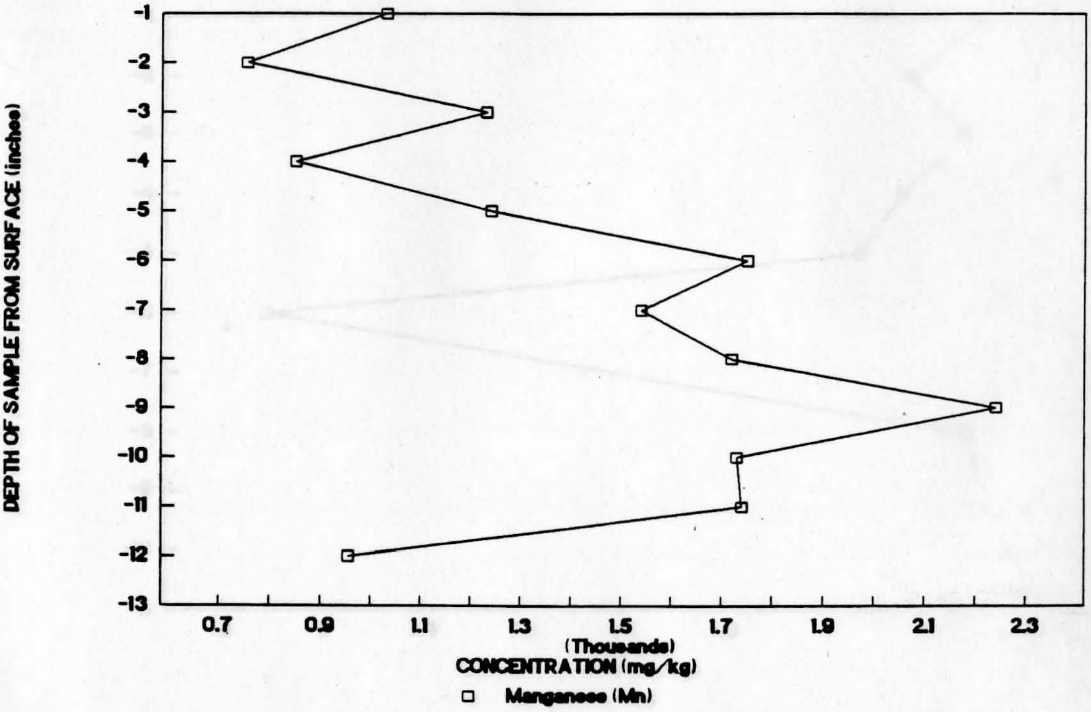


FIGURE 4.67: Manganese Concentrations (mg/kg) Varying With Depth (inches) at the Newton Falls Coring Location (right bank, in vicinity of the Newton Falls water intake line)

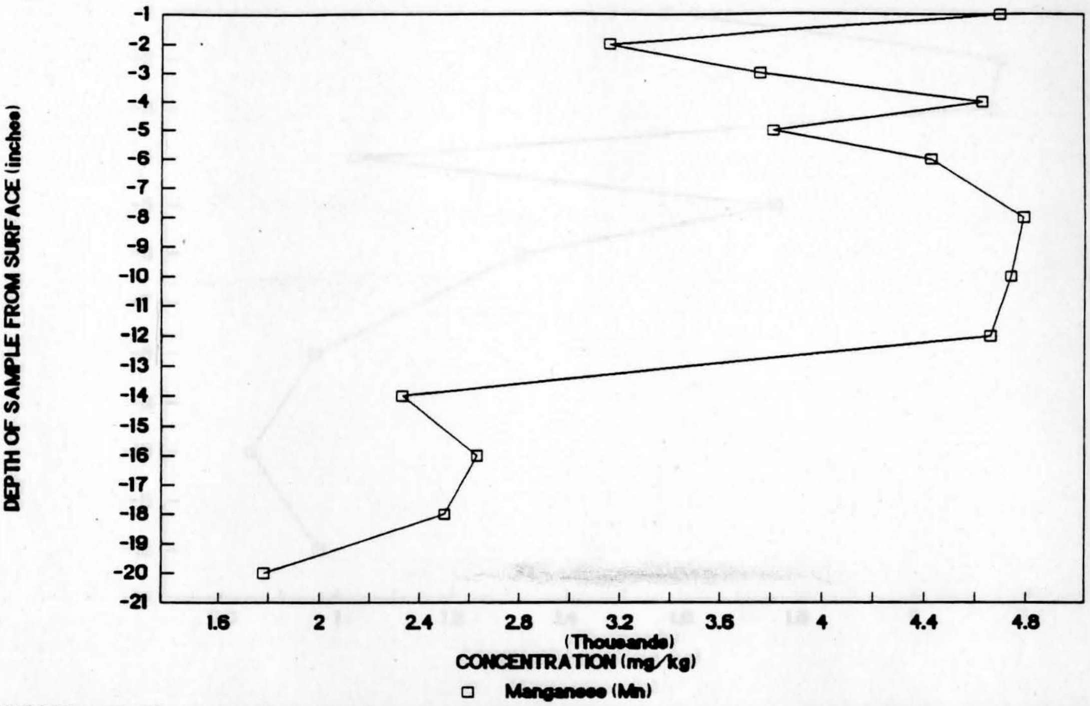


FIGURE 4.68: Manganese Concentrations (mg/kg) Varying With Depth (inches) at the Warren Coring Location (left bank, directly downstream from the Copperweld discharge)

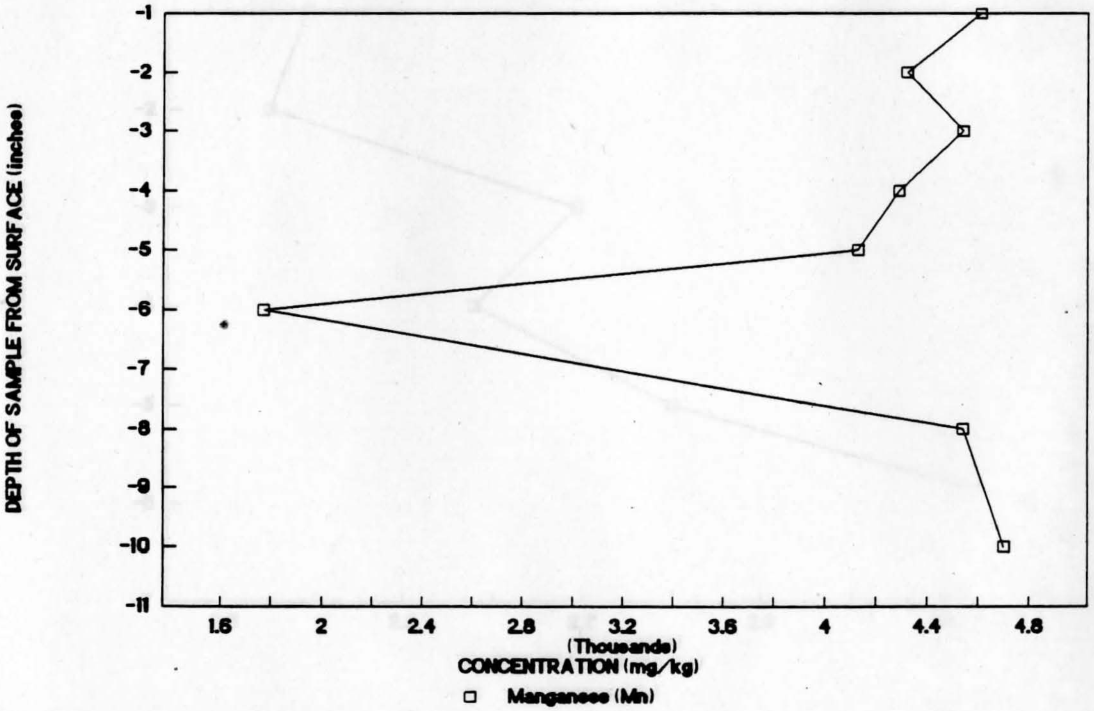


FIGURE 4.69: Manganese Concentrations (mg/kg) Varying With Depth (inches) at the Warren Coring Location (right channel, directly downstream from the Copperweld discharge)

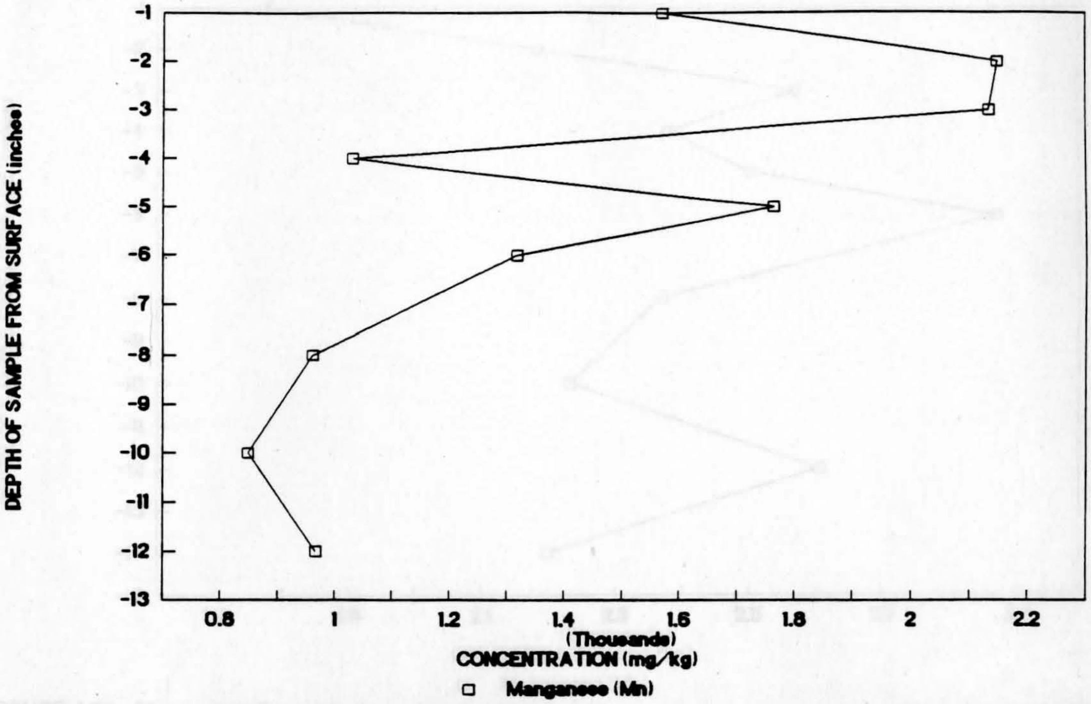


FIGURE 4.70: Manganese Concentrations (mg/kg) Varying With Depth (inches) at the Youngstown Coring Location (left bank, 200 ft downstream from the Youngstown municipal discharge line)

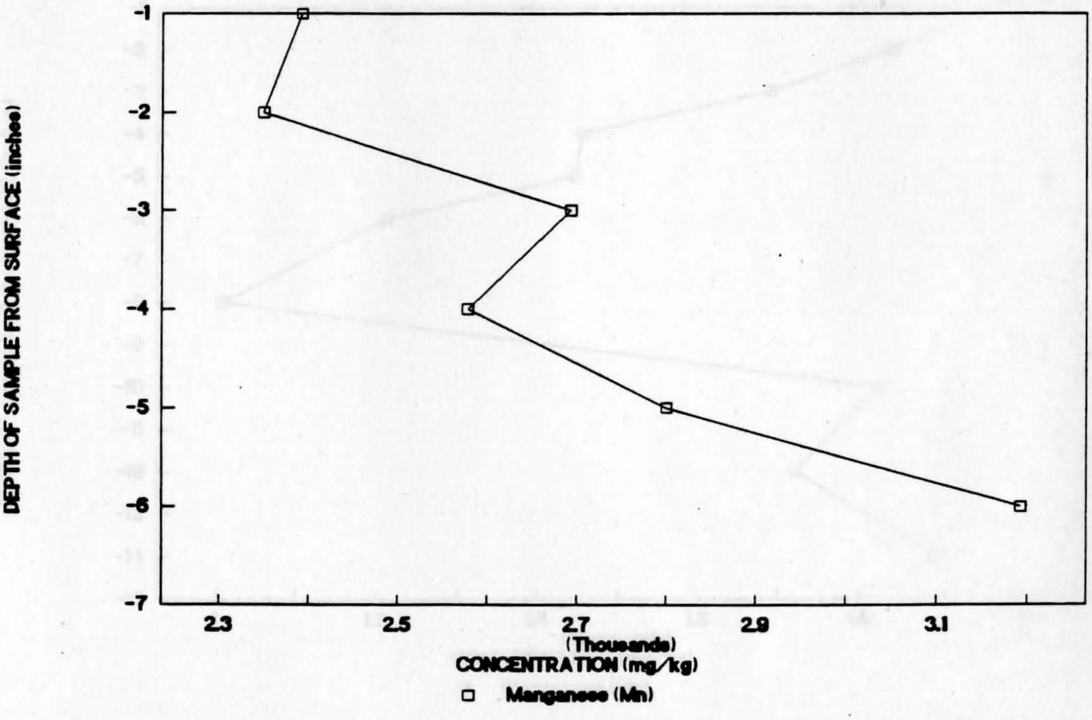


FIGURE 4.71: Manganese Concentrations (mg/kg) Varying With Depth (inches) at the Youngstown Coring Location (center channel, a half mile downstream from the Youngstown municipal discharge)

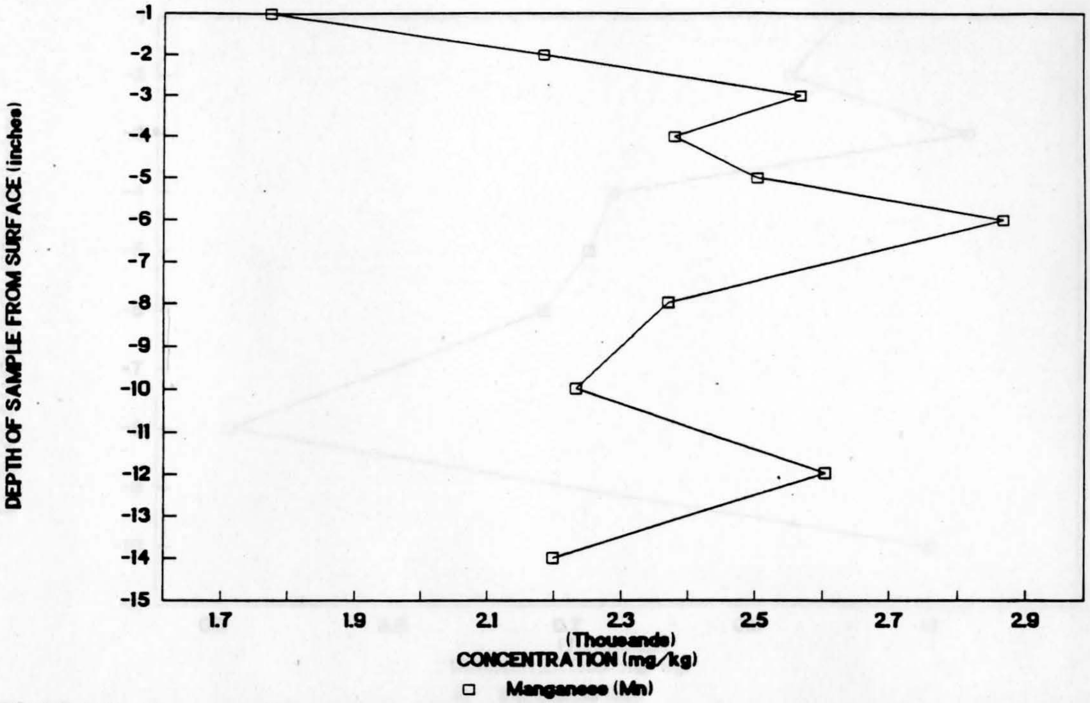


FIGURE 4.72: Manganese Concentrations (mg/kg) Varying With Depth (inches) at the Struthers Coring Location (left bank, directly across from the Struthers municipal discharge culvert)

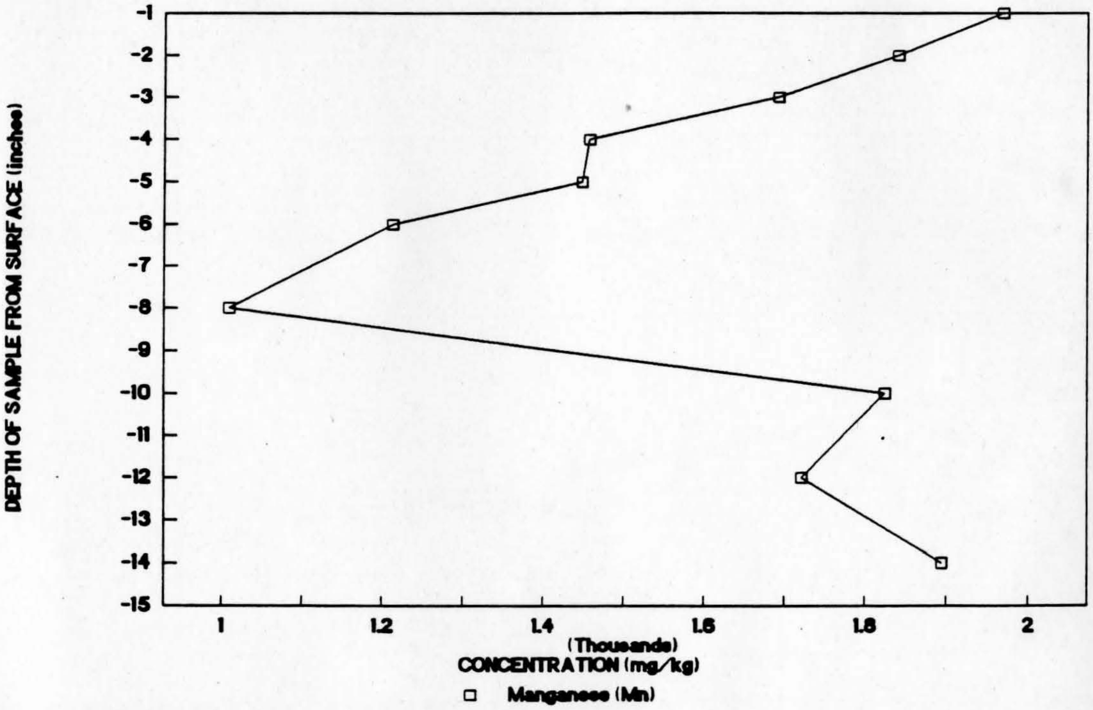


FIGURE 4.73: Manganese Concentrations (mg/kg) Varying With Depth (inches) at the Struthers Coring Location (right bank, 200 ft downstream from the Struthers municipal discharge culvert)

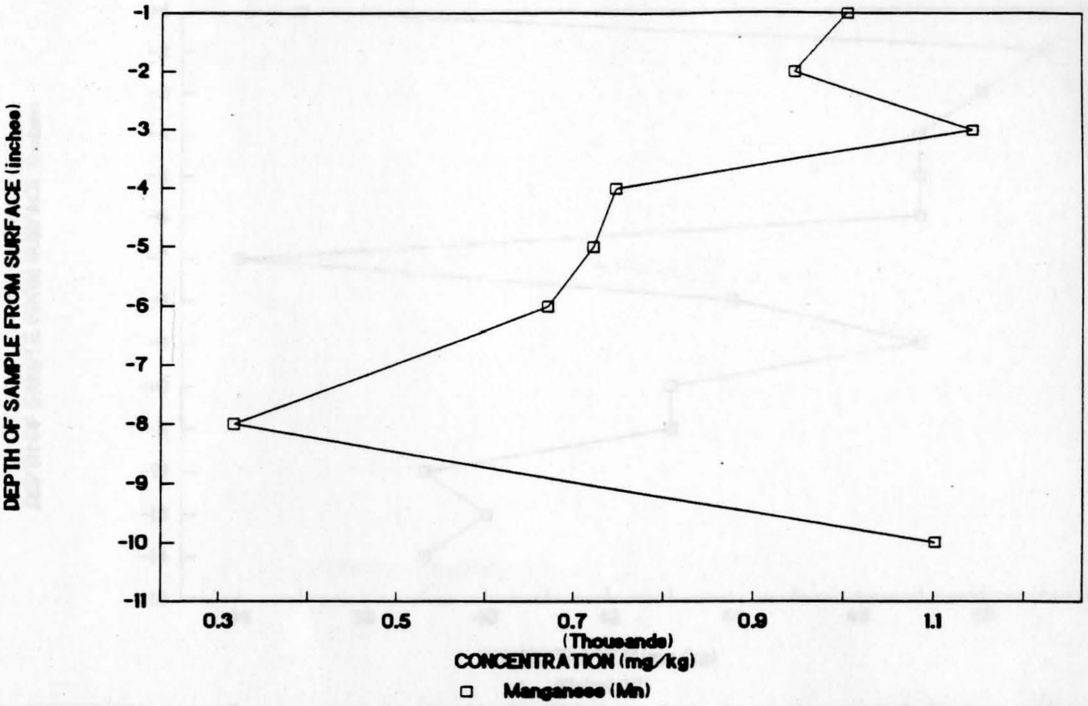


FIGURE 4.74: Manganese Concentrations (mg/kg) Varying With Depth (inches) at the Struthers Coring Location (left bank, a quarter mile downstream from Struthers municipal discharge culvert)

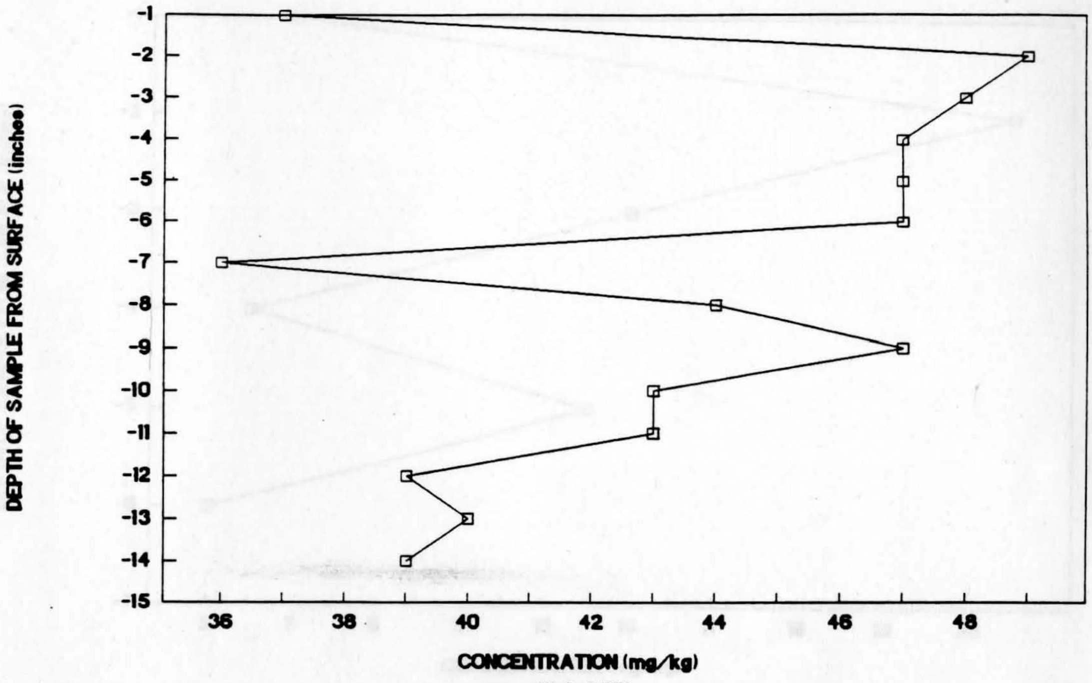


FIGURE 4.75: Nickel Concentrations (mg/kg) Varying With Depth (inches) at the Newton Falls Coring Location (left bank, in vicinity of the Newton Falls water intake line)

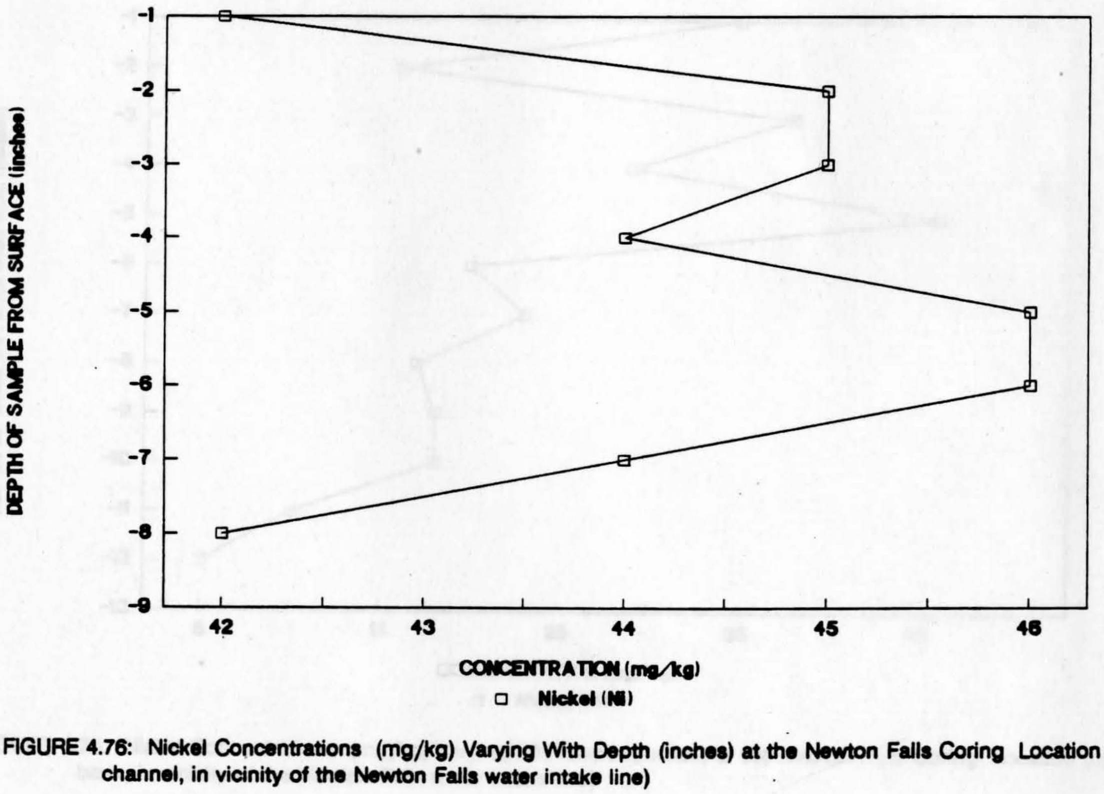


FIGURE 4.76: Nickel Concentrations (mg/kg) Varying With Depth (inches) at the Newton Falls Coring Location (left channel, in vicinity of the Newton Falls water intake line)

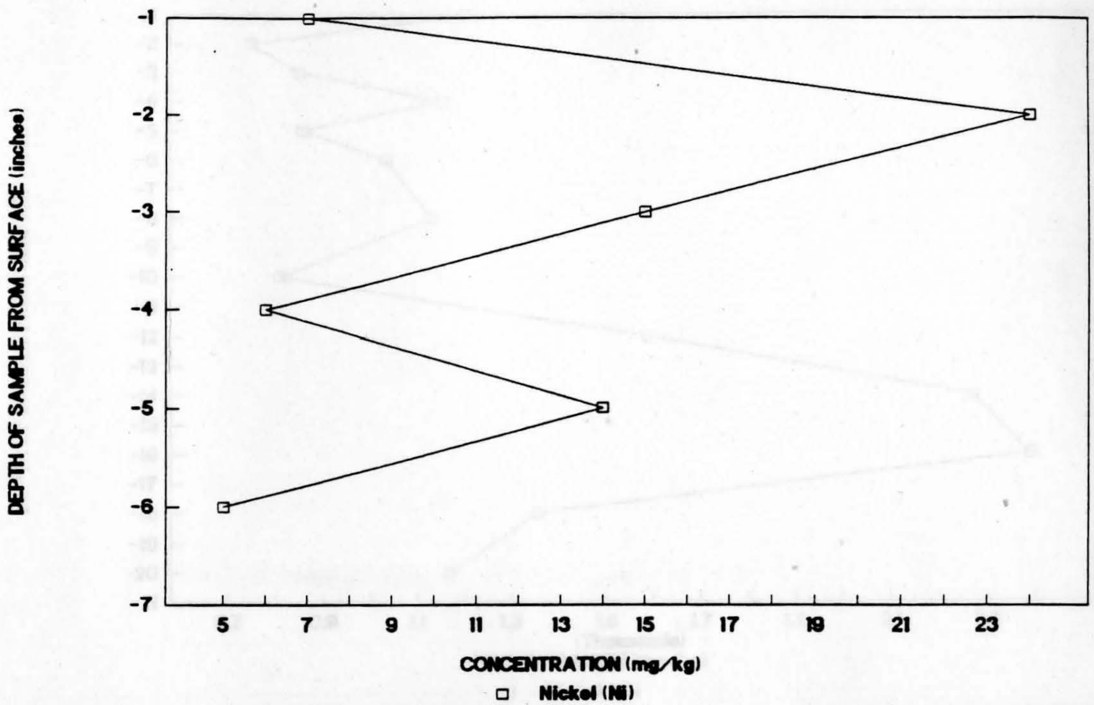


FIGURE 4.77: Nickel Concentrations (mg/kg) Varying With Depth (inches) at the Newton Falls Coring Location (right channel, in vicinity of the Newton Falls water intake line)

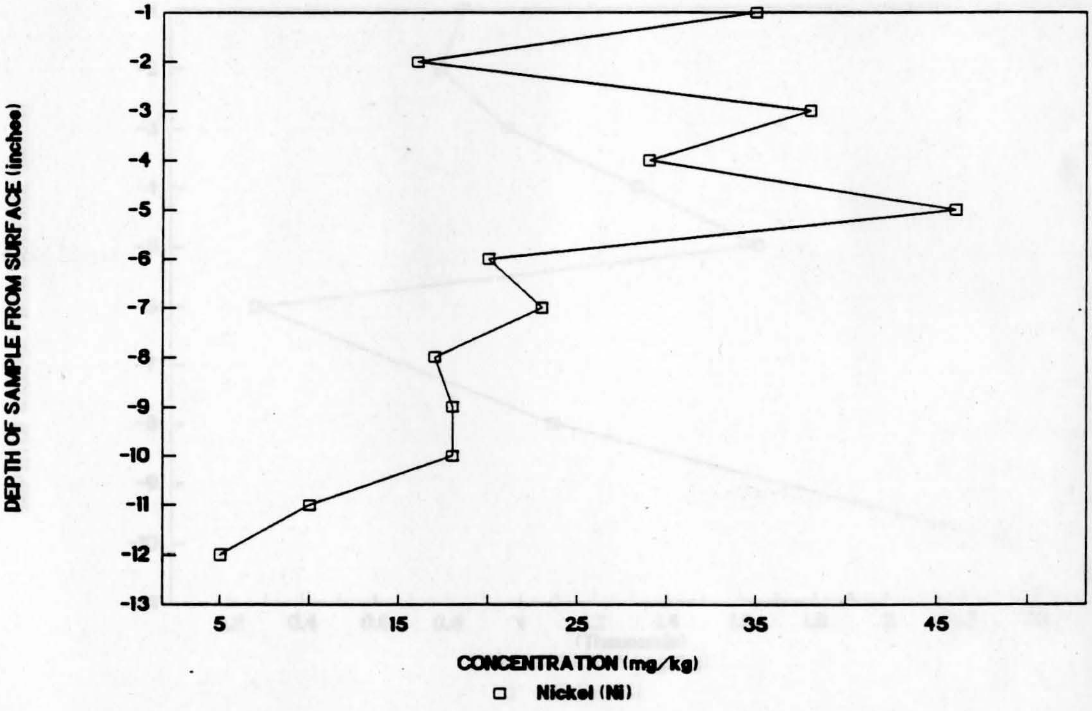


FIGURE 4.78: Nickel Concentrations (mg/kg) Varying With Depth (inches) at the Newton Falls Coring Location (right bank, in vicinity of the Newton Falls water intake line)

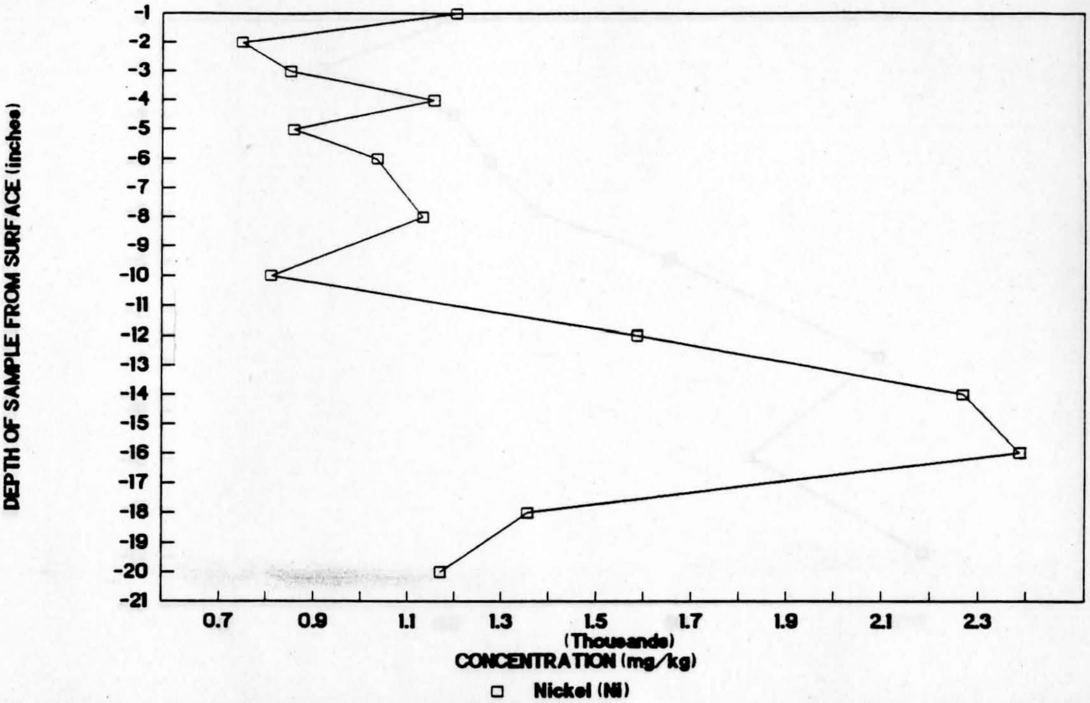


FIGURE 4.79: Nickel Concentrations (mg/kg) Varying With Depth (inches) at the Warren Coring Location (left bank, directly downstream from the Copperweld discharge)

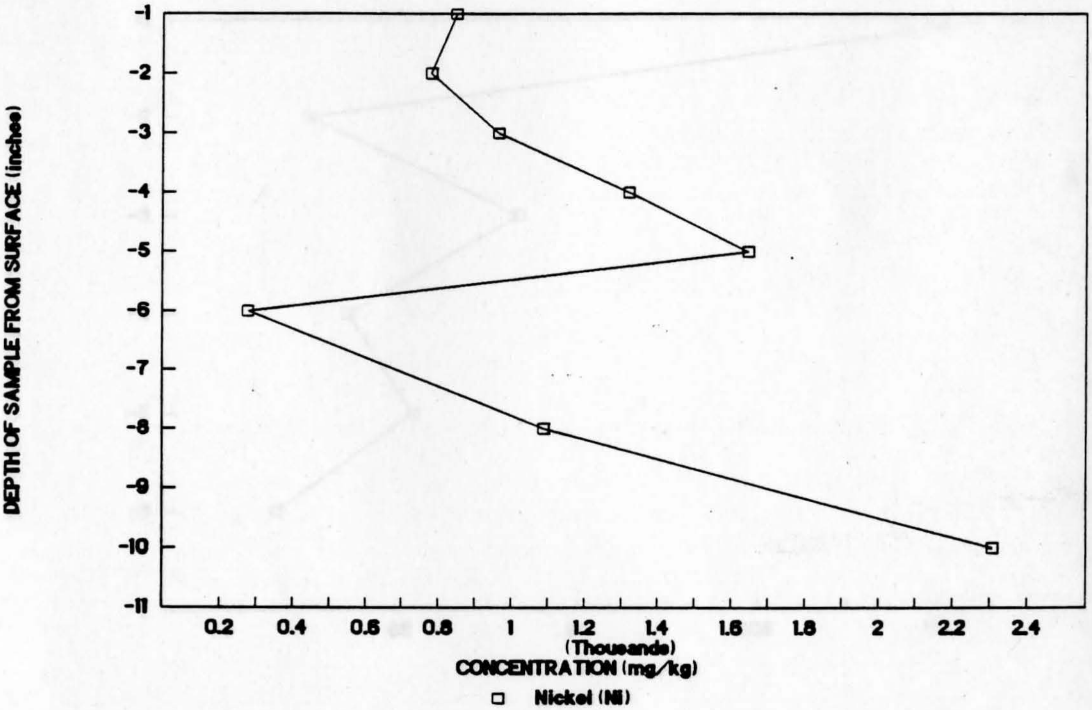


FIGURE 4.80: Nickel Concentrations (mg/kg) Varying With Depth (inches) at the Warren Coring Location (right channel, directly downstream from the Copperweld discharge)

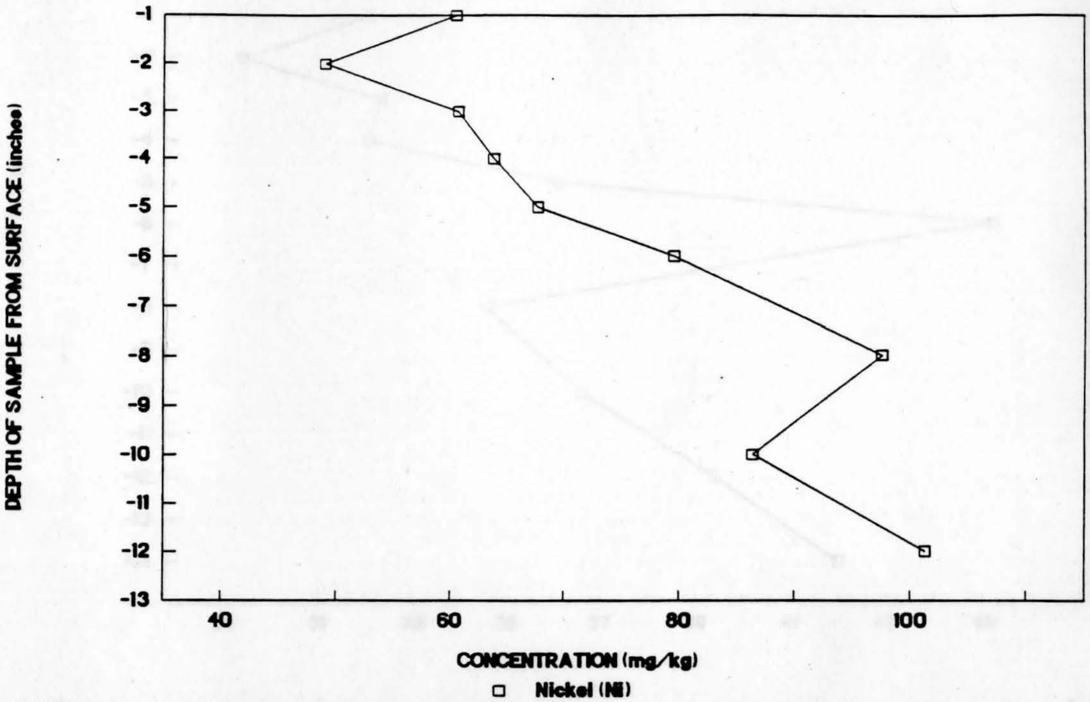


FIGURE 4.81: Nickel Concentrations (mg/kg) Varying With Depth (inches) at the Youngstown Coring Location (left bank, 200 ft downstream from the Youngstown municipal discharge line)

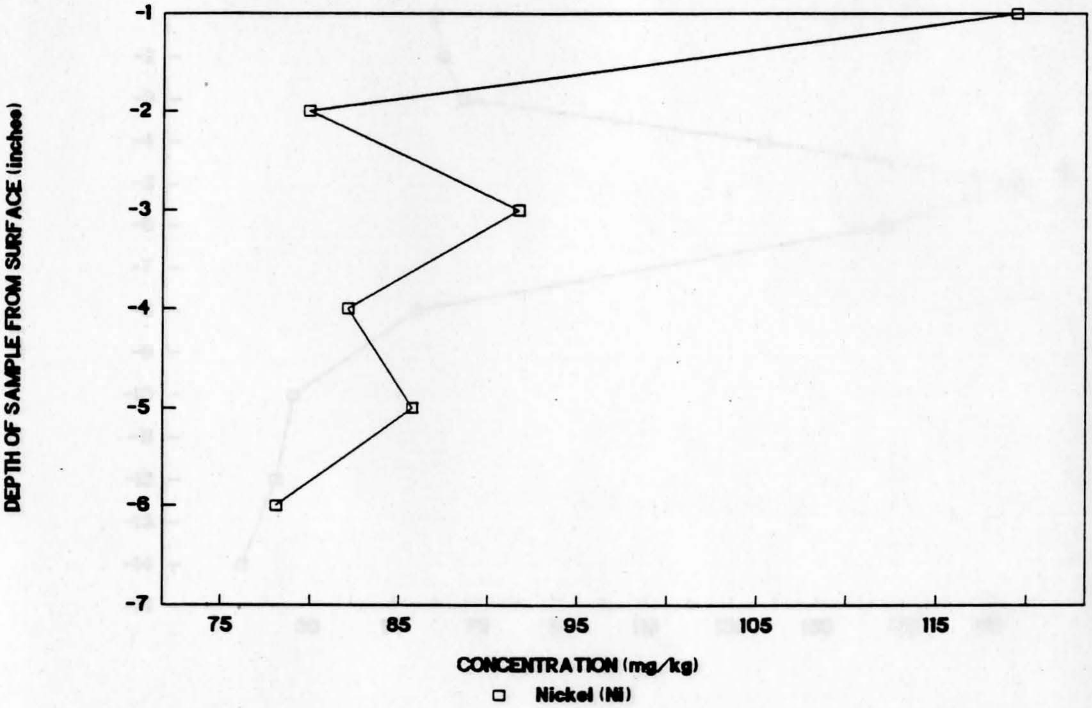


FIGURE 4.82: Nickel Concentrations (mg/kg) Varying With Depth (inches) at the Youngstown Coring Location (center channel, a half mile downstream from the Youngstown municipal discharge)

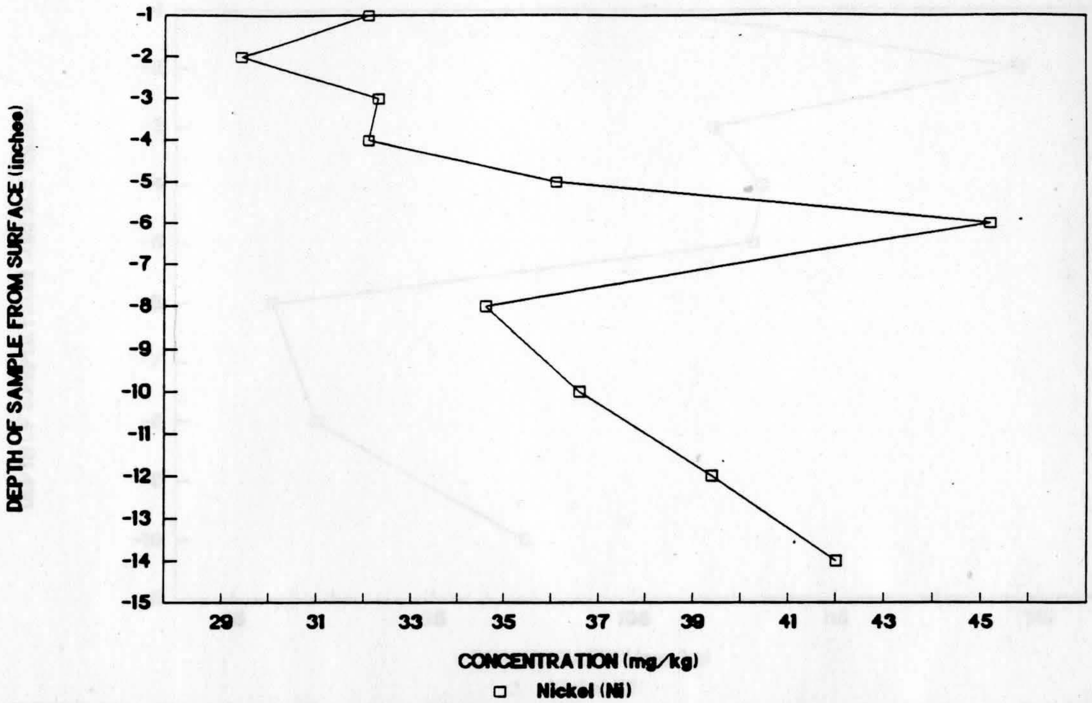


FIGURE 4.83: Nickel Concentrations (mg/kg) Varying With Depth (inches) at the Struthers Coring Location (left bank, directly across from the Struthers municipal discharge culvert)

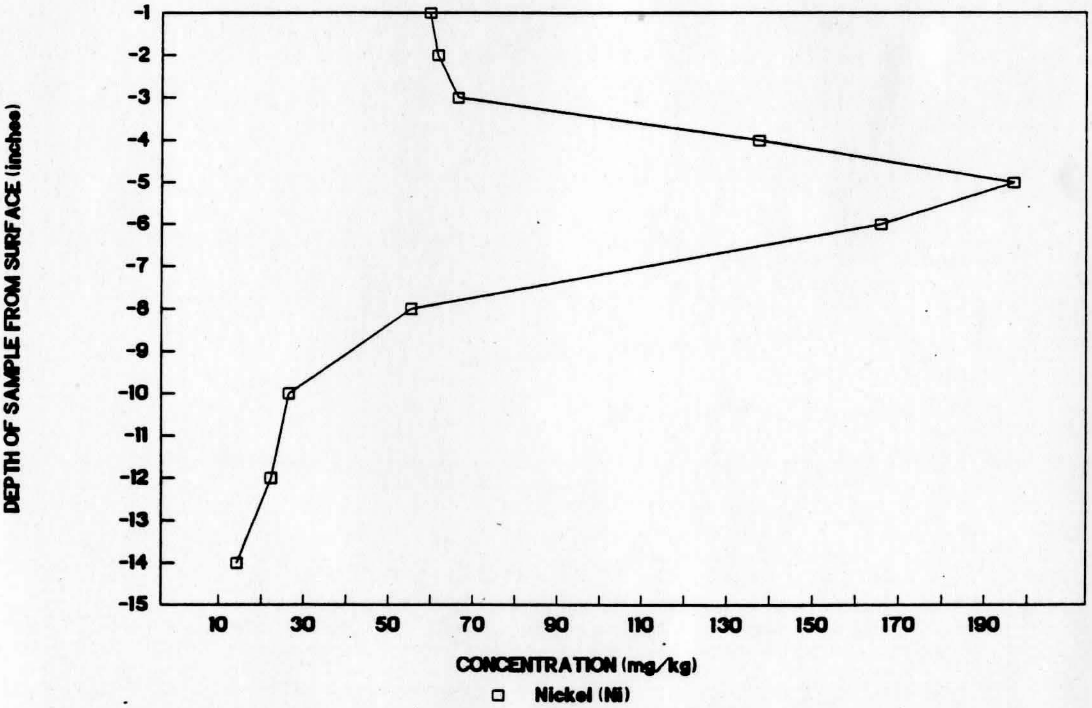


FIGURE 4.84: Nickel Concentrations (mg/kg) Varying With Depth (inches) at the Struthers Coring Location (right bank, 200 ft downstream from the Struthers municipal discharge culvert)

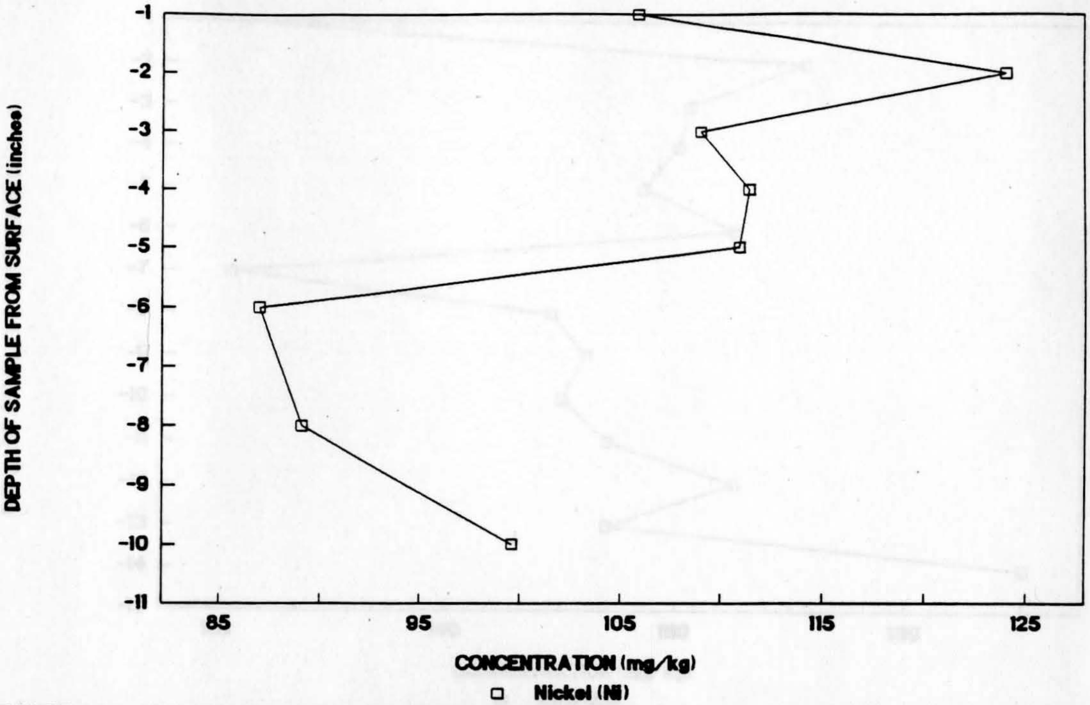


FIGURE 4.85: Nickel Concentrations (mg/kg) Varying With Depth (inches) at the Struthers Coring Location (left bank, a quarter mile downstream from the Struthers municipal discharge culvert)

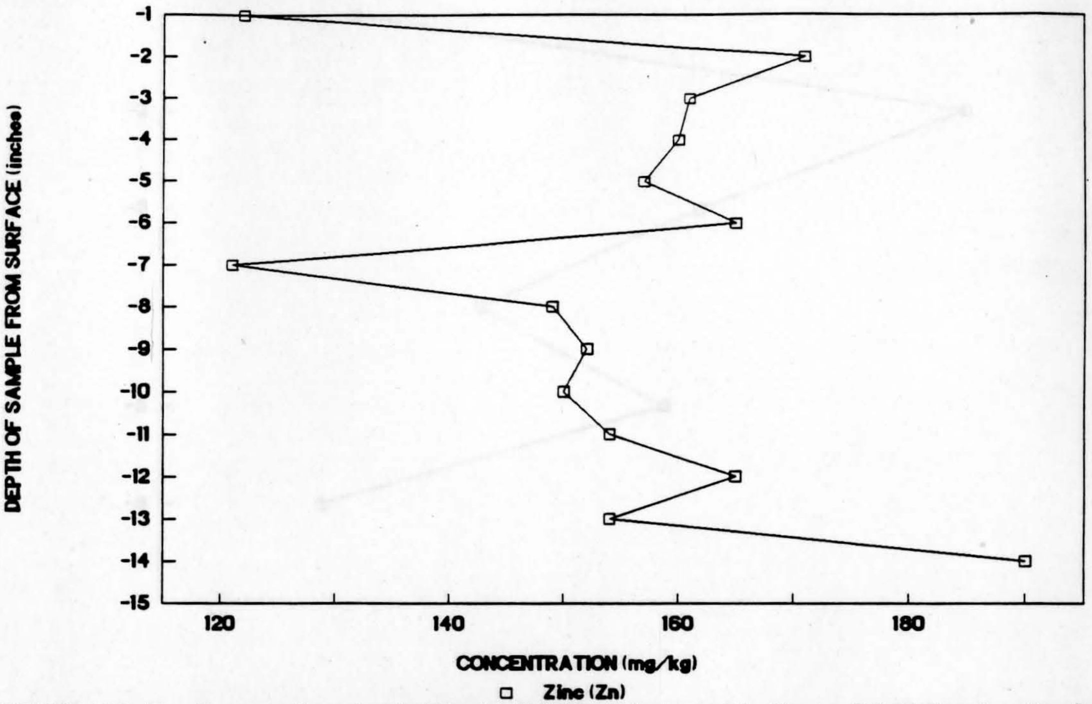


FIGURE 4.86: Zinc Concentrations (mg/kg) Varying With Depth (inches) at the Newton Falls Coring Location (left bank, in vicinity of the Newton Falls water intake line)

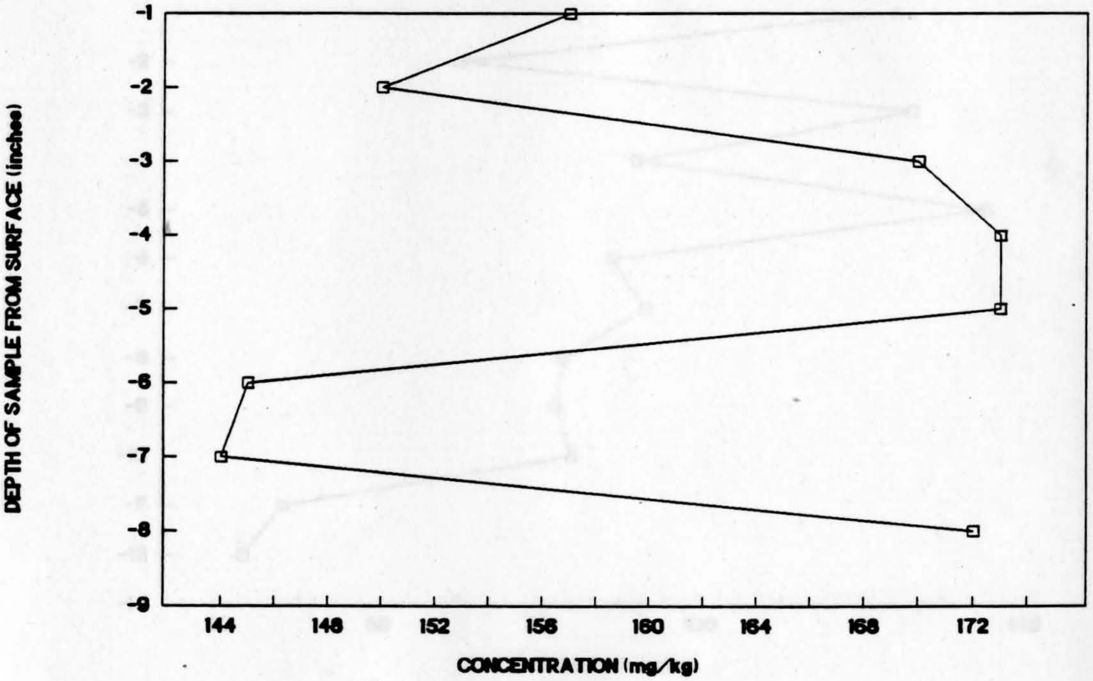


FIGURE 4.87: Zinc Concentrations (mg/kg) Varying With Depth (inches) at the Newton Falls Coring Location (left channel, in vicinity of the Newton Falls water intake line)

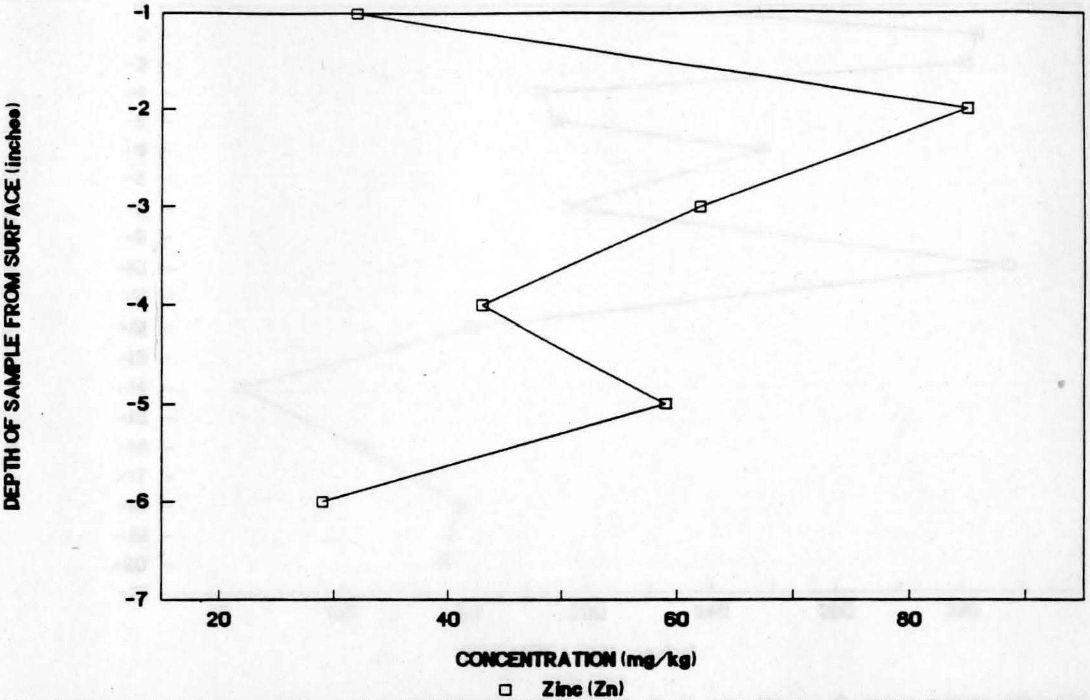


FIGURE 4.88: Zinc Concentrations (mg/kg) Varying With Depth (inches) at the Newton Falls Coring Location (right channel, in vicinity of the Newton Falls water intake line)

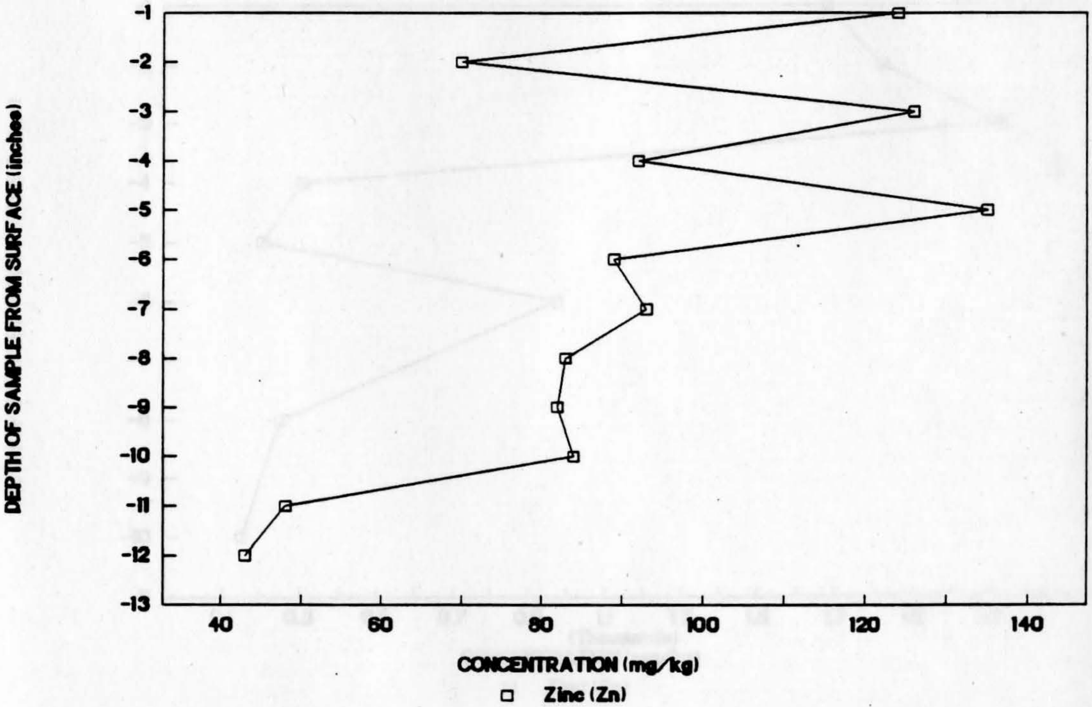


FIGURE 4.89: Zinc Concentrations (mg/kg) Varying With Depth (inches) at the Newton Falls Coring Location (right bank, in vicinity of the Newton Falls water intake line)

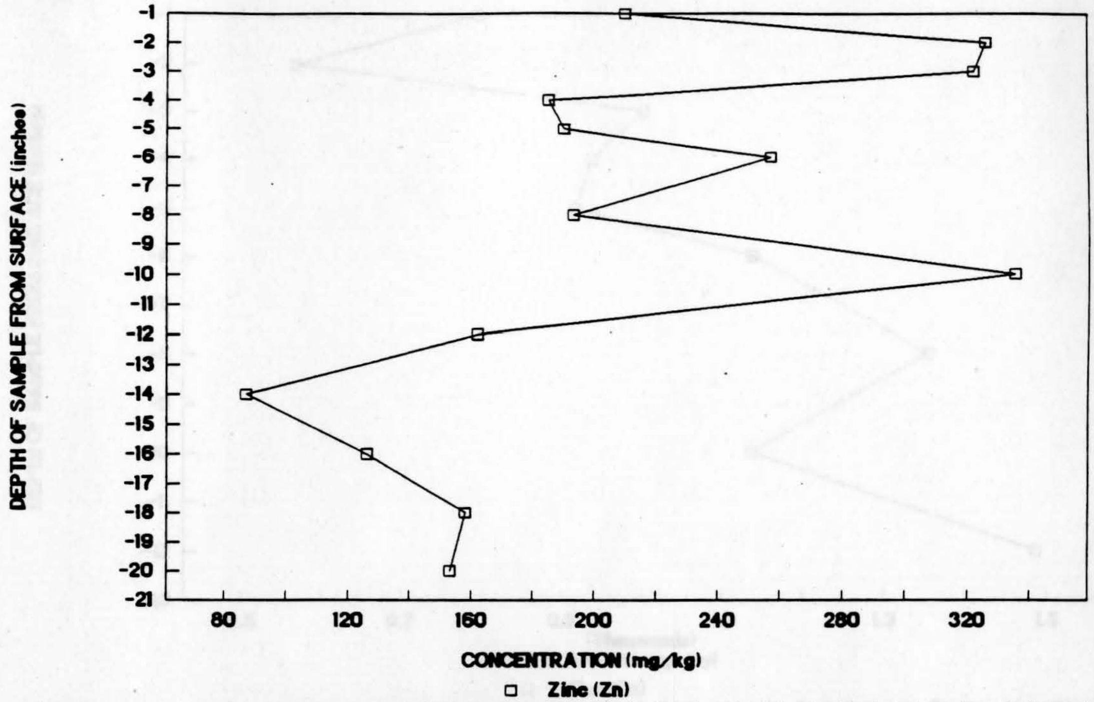


FIGURE 4.90: Zinc Concentrations (mg/kg) Varying With Depth (inches) at the Warren Coring Location (left bank, directly downstream from the Copperweld discharge)

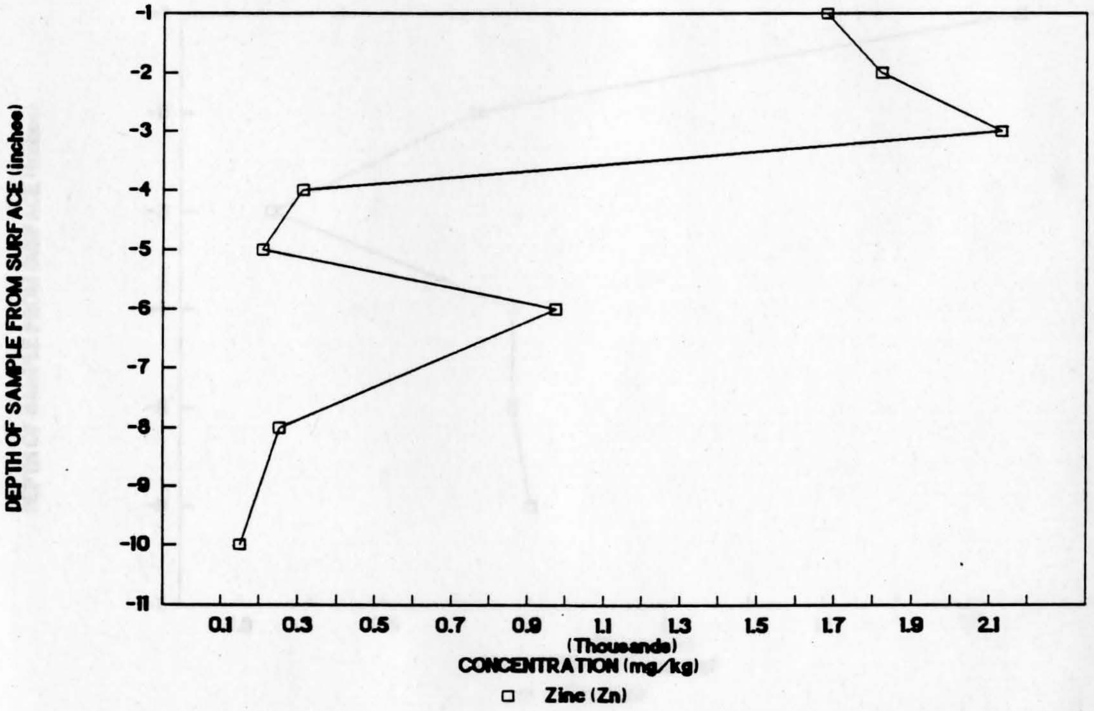


FIGURE 4.91: Zinc Concentrations (mg/kg) Varying With Depth (inches) at the Warren Coring Location (right channel, directly downstream from the Copperweld discharge)

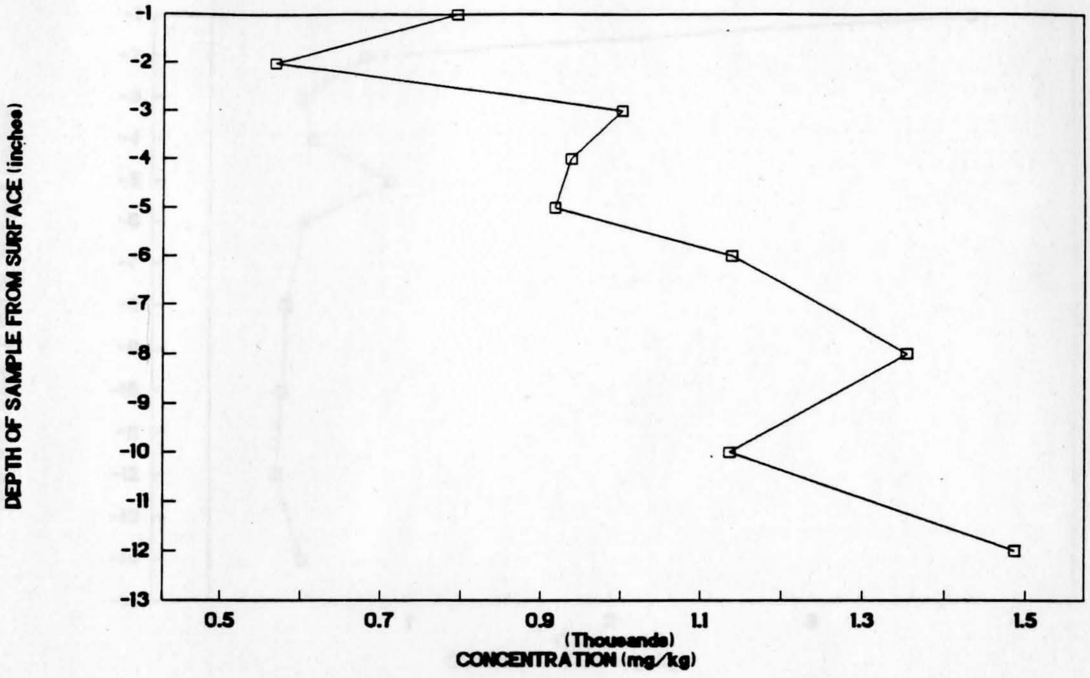


FIGURE 4.92: Zinc Concentrations (mg/kg) Varying With Depth (inches) at the Youngstown Coring Location (left bank, 200 ft downstream from the Youngstown municipal discharge line)

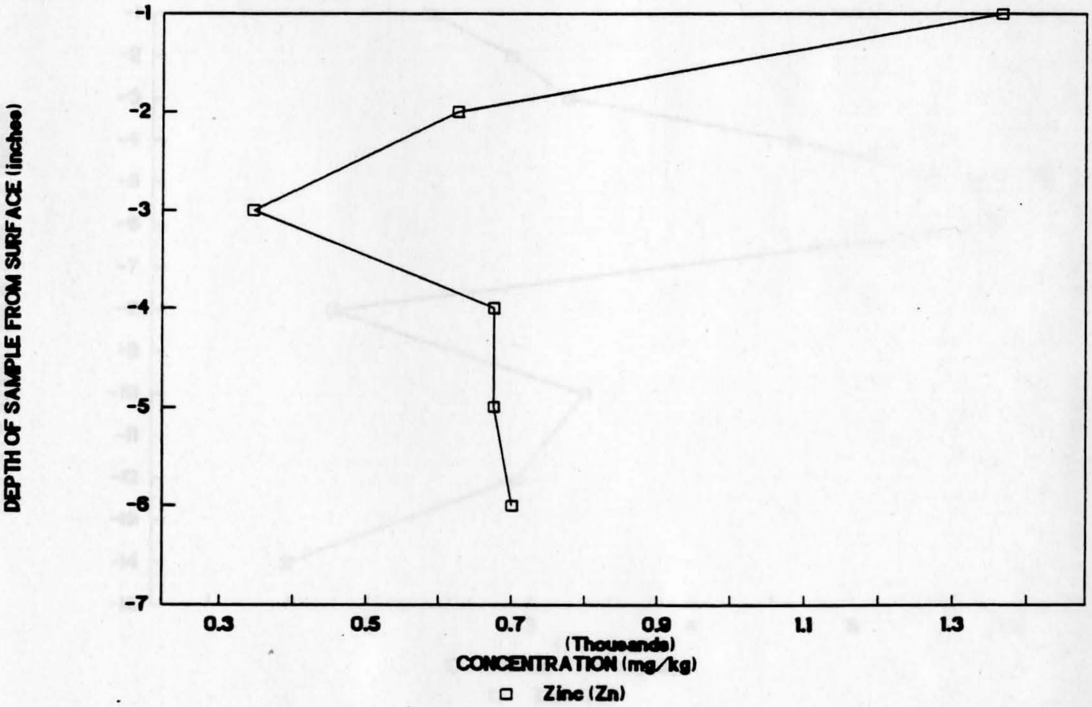


FIGURE 4.93: Zinc Concentrations (mg/kg) Varying With Depth (inches) at the Youngstown Coring Location (center channel, a half mile downstream from the Youngstowns municipal discharge)

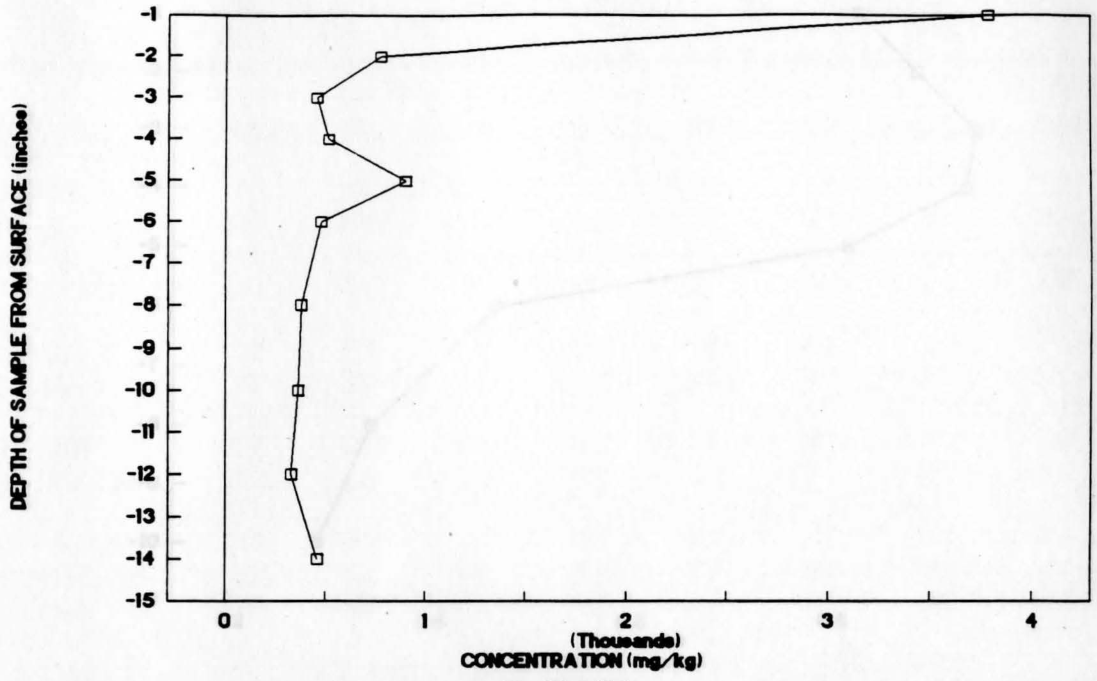


FIGURE 4.94: Zinc Concentrations (mg/kg) Varying With Depth (inches) at the Struthers Coring Location (left bank, directly across from the Struthers municipal discharge culvert)

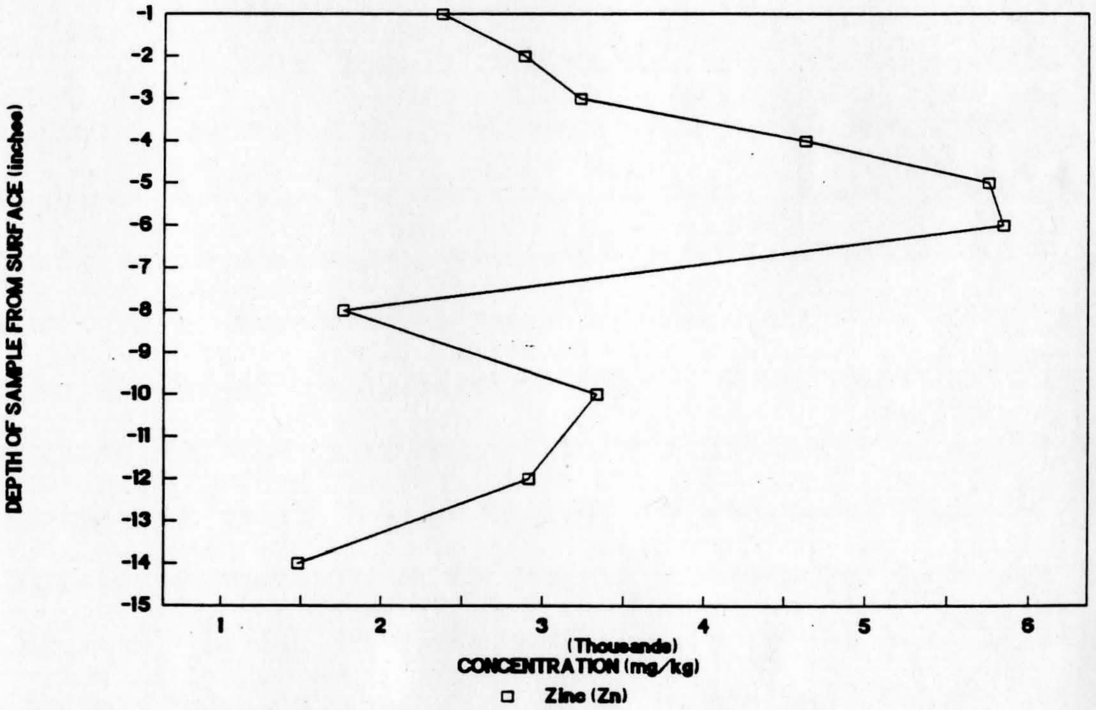


FIGURE 4.95: Zinc Concentrations (mg/kg) Varying With Depth (inches) at the Struthers Coring Location (right bank, 200 ft downstream from the Struthers municipal discharge culvert)

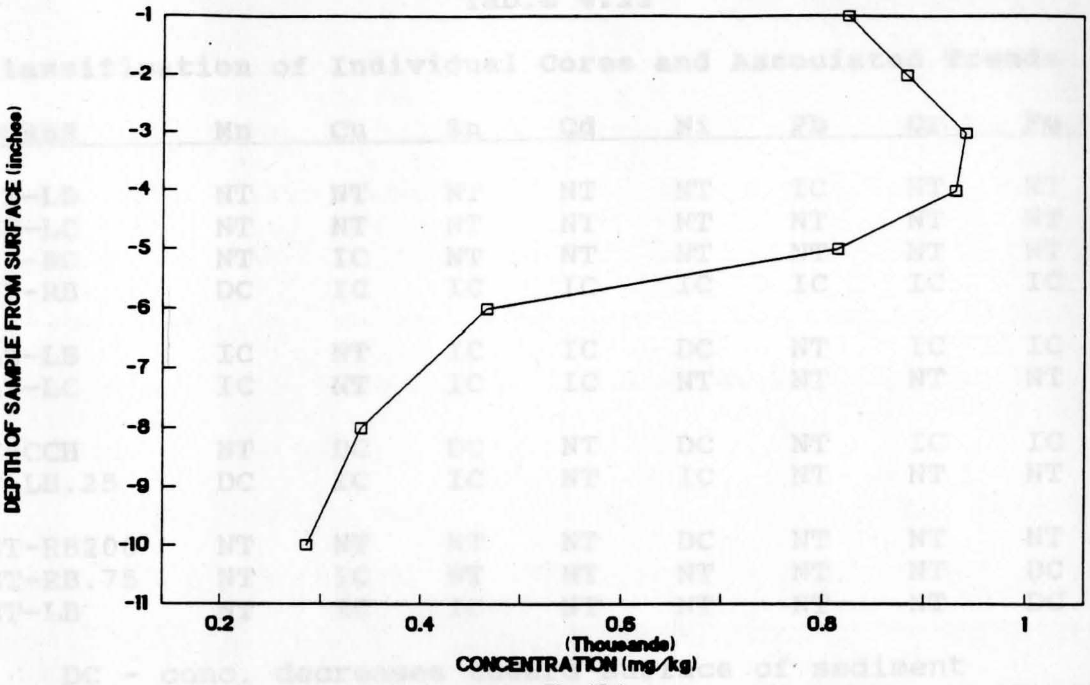


FIGURE 4.96: Zinc Concentrations (mg/kg) Varying With Depth (inches) at the Struthers Coring Location (left bank, a quarter mile downstream from the Struthers municipal discharge culvert)

Table 4.13

Classification of Individual Cores and Associated Trends

CORES	Mn	Cu	Zn	Cd	Ni	Pb	Cr	Fe
NF-LB	NT	NT	NT	NT	NT	IC	NT	NT
NF-LC	NT	NT	NT	NT	NT	NT	NT	NT
NF-RC	NT	IC	NT	NT	NT	NT	NT	NT
NF-RB	DC	IC	IC	IC	IC	IC	IC	IC
LZ-LB	IC	NT	IC	IC	DC	NT	IC	IC
LZ-LC	IC	NT	IC	IC	NT	NT	NT	NT
Y-CCH	NT	DC	DC	NT	DC	NT	IC	IC
Y-LB.25	DC	IC	IC	NT	IC	NT	NT	NT
ST-RB200	NT	NT	NT	NT	DC	NT	NT	NT
ST-RB.75	NT	IC	NT	NT	NT	NT	NT	DC
ST-LB	NT	IC	IC	NT	NT	NT	NT	DC

DC - conc. decreases toward surface of sediment
IC - conc. increases toward surface of bottom sediment
NT - no distinct trend in metal conc. with depth

The most common observation for the core data, as indicated by Table 4.13, was that the metal levels follow no distinct trend. The variation in metal concentrations with depth is inconsistent, with some profiles showing increases and others decreases in metal levels. Although most of the samples showed no distinct trend in metal levels, a larger portion of the samples which did follow a trend showed increasing metal levels toward the sediment surface. The increasing trends seen in some of the samples indicate that the metal levels in the river have increased more recently, possibly due to higher loading conditions. Some of the samples also showed a decreasing trend in metal levels, which suggests lower loading rates in more recent times.

In the sections of the river upstream of Warren, and in the vicinity of the state line, the metal profiles generally showed no distinct trend. In a few of the sample taken from these two locations, an increasing trend was noticed. In the samples taken from the industrialized section of the river, a larger percentage of the samples showed an increasing trend, compared to the samples taken in the "clean" sections of the river.

The core samples were also analyzed to determine whether any variation in metal levels exist with channel cross-section. Based on the tabulated results, a majority of the samples show similar trends across the cross-section. A few of the samples show some differences in metal level trends over a cross-section, but the largest portion show a similar trend. Although some of the core samples do show distinct trends in metal levels, the inconsistency of the results makes it difficult to assign any single classification to the overall trend.

Even more difficult is the attempt to explain why these results exist. If a more distinct trend existed, for example a net increase toward the sediment-water interface, this may suggest that the dischargers to the river are contributing increased amounts of metal loadings to the river in recent years. A net decrease on the other hand may suggest that the metal loadings to the river have decreased over the years. Based on the results of this study, there has been no noticeable improvement in the quality of the Mahoning River bottom sediments.

Classification of Contaminant Levels

Based on the data generated in this study, Mahoning River sediments can be classified as to their degree of pollution with each heavy metal using the criteria proposed by the USEPA (16) and Kelly & Hite (2). Table 4.14 represents the classification of the industrialized and non-industrialized sections of the river based on both of these systems. The Mahoning River sediments metal levels fall into a range of the classifications.

Table 4.14
Ranges for Grab Sample Classifications Based on Both the USEPA and Kelly & Hite Classification.

	Kelly & Hite Class.		USEPA Class.	
ELEMENT	Non indust. **Section**	Industr. **Section**	Non-industr. **Section**	Industr. **Section**
Mn	A-D	A-D	A-C	C
Cu	A-B	B-E	A-B	C
Zn	A-D	B-E	A-B	C
Cd	A-E	A-E	A-C	A-C
Ni			B-C	B-C
Pb	A-C	D-E	A-B	C
Cr	A-C	A-E	A-B	B-C
Fe	A-C	A-E	A-C	A-C

A - Non-elevated
B - Slightly elevated
C - Elevated
D - Highly-elevated
E - Extreme

A - Non-polluted
B - Moderately Polluted
C - Heavily Polluted

CADMIUM: Cadmium concentrations in the grab samples were mostly rated in the nonelevated range since a majority of the samples did not register any cadmium present. However, the cutoff concentrations for the slightly elevated and elevated classifications were below the detection limit in this study. Of the grab samples which did register some cadmium present, all classified in the elevated to the highly elevated range based on the Kelly & Hite scale. The core samples which showed the presence of cadmium were also in the elevated to extreme range for Kelly & Hite. There was only one cadmium classification for the USEPA rating, and the majority of the samples were below the 6.0 mg/kg level, thus remaining below the heavily polluted classification. The maximum cadmium level encountered during the river study was 7.80 mg/kg at the Warren coring location, which exceeded the maximum limits for the most polluted category on both scales.

CHROMIUM: Chromium levels recorded in the grab samples showed a range of classifications. Upstream of Warren, the chromium concentrations fell between the non-elevated and elevated classifications in the Kelly & Hite scale. In the industrialized section of the river, the chromium concentrations were mostly above the highly elevated concentration limit. For the USEPA classification, the section of the river upstream of Warren, and closer to the state line, showed chromium levels mostly in the moderately polluted range. However, the chromium concentrations in the industrialized section of the river classified as heavily polluted by the USEPA standards.

COPPER: Copper concentrations in the industrialized section of the river typically classified as either highly elevated or extremely elevated based on Kelly & Hite's ratings. Only a few scattered locations in this section showed concentrations of copper below the highly elevated limit of 100 mg/kg. Based on the USEPA rating, the entire section of the river downstream of Warren classified as being heavily polluted. Copper levels above Warren all fell within the two least polluted categories in both classification schemes.

IRON: Iron concentrations in the river also covered a range of classifications for both scales. Based on the Kelly & Hite scale, the iron concentrations rated from below the nonpolluted levels, to over four time higher than the cutoff for extreme concentrations. For the USEPA rating, some of the samples fell within the moderately polluted range, while a majority exceeded the heavily polluted range. Some of the sample had iron concentrations which were ten times higher than the heavily polluted limit of 25,000 mg/kg. The heavily polluted and extreme concentrations of iron were mostly encountered in the portion of the river where the steel mills had been or still are located.

LEAD: Lead concentrations followed the same trend as did the copper concentrations. For the USEPA scale and the Kelly & Hite scale, the concentrations of lead encountered in the section of the river downstream of Warren exceeded the heavily polluted and extreme classifications, respectively. In the section of the river upstream of Warren, the lead concentrations were rated as being elevated or lower by Kelly & Hite, and as non-polluted by the USEPA.

MANGANESE: The manganese levels found throughout the entire course of the river sampled rated as heavily polluted by the USEPA scale. As for the Kelly & Hite scale, the concentrations encountered covered the range from nonpolluted to highly elevated. The majority of samples fell into the non-elevated range upstream of Warren and in the slightly elevated to elevated range in the industrialized section.

NICKEL: Nickel concentrations could only be compared to the USEPA scale, since a classification did not exist for Kelly & Hite. Nickel, like most of the metals discussed previously, showed levels in the section of the river upstream of Warren which were either at or below the moderate pollution limit. As the river continued on into the Warren section, the nickel levels were maintained above the heavily polluted concentration limits.

ZINC: The zinc concentrations encountered in the river covered the entire rating scales for both the Kelly & Hite and USEPA ratings. The lower classifications were encountered upstream of Warren, while the elevated, or heavily polluted concentrations were encountered downstream of Warren.

Although a few of the metal concentrations encountered in the Mahoning River are below the lower limits of both the

Kelly & Hite and USEPA rating scale, the overall rating of sediment in the industrialized section of the river would classify as elevated to extremely elevated or heavily polluted. Based on these classifications, the river sediments in the Mahoning River will require a long period of time before the levels throughout the entire river's course will be classified as non-elevated or non-polluted. The overall reduction in metal loadings to the Mahoning River has benefitted the river water column, but improvement of the river bottom sediments has not yet occurred to any significant extent.

CHAPTER V

CONCLUSIONS:

Over the past decade the metal loadings to the Mahoning River have been reduced both through governmental enforcement and closing of the surrounding industries. These factors have resulted in decreases in water column concentrations of heavy metals. However, the river bottom sediments are still contaminated with high levels of several heavy metals.

The absence of municipal and industrial discharge sources upstream of Warren, Ohio allowed the background levels of eight metals (cadmium, chromium, copper, iron, lead, manganese, nickel and zinc) to be established. Analyses performed on sediment grab samples collected between Newton Falls, Ohio and the Pennsylvania state line showed similar results for most of the metals. Concentrations were low upstream of Warren, but increased abruptly in the industrialized section of the river.

The grab samples suggest that the presence of the various dischargers contribute significantly to the levels of metals within the Mahoning River. The metal levels found within the Mahoning show that the river bottom sediments are still heavily polluted. Applying criteria developed by Kelly

& Hite (2), bottom sediments upstream of Warren mostly contained "non-elevated" to "slightly elevated" levels of heavy metals, while concentrations in the industrialized section of the river were mostly classified as "elevated" to "extreme". The analysis of core samples did not provide sufficient evidence to determine whether sediment heavy metal levels are slowly improving, or progressively getting worse. The majority of heavy metal profiles showed no noticeable trend in concentration as a function of depth in the bottom sediments. Based on the core results, additional analysis is required before any real determination can be made. However, it appears that no significant decrease in sediment metal concentrations has occurred within the past decade. Finally, the data generated in this study suggest that the Mahoning River will require a very long period (at least several decades) of reduced heavy metal loadings for the course of nature to return the river to its prior preindustrial state.

APPENDIX A

CORING LOCATION SITE DESCRIPTION

Newton Falls, Ohio

The core and grab samples were taken (July, 1989) in the vicinity of the Newton Falls water treatment plant intake. The current in this portion of the river was flowing at a slightly greater velocity than normally expected. The higher flow velocity resulted from excessive rainfall during the months of May and June. As a result of the above-normal rainfall, the reservoirs which fed the Mahoning had very high water levels and they provided a continual flow of water. Initial probing of the banks and channel of the river suggested that the entire cross-section was solid rock. Very little sediment was obtainable using the grab sampler. What sediment was brought up from the river channel contained small rock particles.

But, further probing of the river bottom produced sediment deposits varying from a few inches, up to 20 inches deep. The deposits which provided the greatest depths were located along the bends, within the river channel where a drop in water velocity occurred as a result of the channel geometry. Both the right and left banks provided sediment deposits exceeding 14 inches of very fine silty deposits. The core samples taken in the left and right channels provided core samples of 6 and 8 inches, respectively. Samples taken from the river channel showed a larger particle size. Channel sediment appeared to have a consistency similar to sand, while the bank cores had a more silty particle base. Scouring was expected to be a major factor controlling the particle size distribution found to exist along the cross-section of the river. Generally larger particles settled in the channel where the water velocity was more rapid, much smaller particles were found near the river banks, where water velocity dropped considerably.

Warren, Ohio (near Luntz Corp.)

The Warren, Ohio sampling site was located across North River Road from the Luntz Corporation (Luntz), just downstream from Copperweld Steel Corporation (Copperweld) of Warren. This area of the river was suspected to have been highly contaminated with heavy metals, due to the largely metals-based industry located along this portion of the river. Access to the river was difficult, because of steeply-sloped 20 to 30 foot-high river banks. The water velocity in this portion of the river was somewhat more rapid than that previously encountered in Newton Falls. The swift current made entry into the river difficult. (The electric motor on the flat-bottom rowboat proved to be a valuable asset travelling against the current.)

The banks and channels along this portion of the river were extremely rocky. Small deposits of sediment were located along the cross-section of the river, but it was insufficient to obtain a grab sample. The channel in this section of the river was only 2 to 4 feet deep and somewhat wider than upstream. Due to the channel geometry, the effects of scouring played a major role in keeping the river channel free of sediment deposits. Even along the river banks, the effects of scouring were evidenced by the small amounts of sediment found. Grab samples were taken along the right bank, right channel, and left channel. All three grab samples contained small pebbles and larger granular particles. Along the left bank of the river, an industrial discharger was located upstream from where the two channel grab samples were taken. The right bank grab sample was taken directly across from the Copperweld discharge outlet on the opposite bank. The right bank sample was taken as a representative sample independent of the industrial discharger's influence. The left bank of the river was probed for an ideal location for a possible core sample.

The left bank was also expected to show a rocky composition produced by scouring, similar to that found in the cross-section of the river. Initially, the left bank seemed to follow suit, but closer to the discharge pipe, the portion of the bank following an inward bend in the river was found to contain a large sediment deposit. The deposit was located approximately 200 feet downstream from the discharge, at a location where the river had a lower velocity. Here, the sediment deposit was approximately 36 inches deep and very dark and fine-grained in appearance. The water level in this section of the river was approximately 10 to 14 feet deep, much deeper than the 2- to 4-foot levels found in the river this section of the river. (Author's Note: As a child, this is the section of the river I remember most, and all that I remember was a flowing mass of murky water which produced a horrid odor during the summer months). The banks and channels along this stretch of the river are almost identical to those encountered along the Youngstown section. A rocky channel with very little sediment deposit was found, and the only significant amounts of sediment were located within 3 to 4 feet of the banks.

Channel depth varied only slightly, with 4-to 6-foot depths being most frequent. There were various locations where slight rapids had formed due to a wide, shallow channel. The core samples taken from the banks also had an elevated level of petroleum products and a greasy texture. Samples were taken at various locations along the banks, approximately 100 feet, a quarter mile, and a half mile downstream of the Struthers Wastewater Treatment Plant discharge pipe.

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