

HEAVY METALS IN WATER, SEDIMENTS, AND  
CHIRONOMIDS IN A STREAM RECEIVING  
DOMESTIC AND OIL REFINERY  
EFFLUENTS

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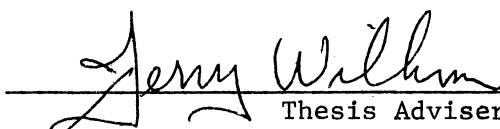
Submitted to the Faculty of the Graduate College  
of the Oklahoma State University  
in partial fulfillment of the requirements  
for the Degree of  
DOCTOR OF PHILOSOPHY  
May, 1975


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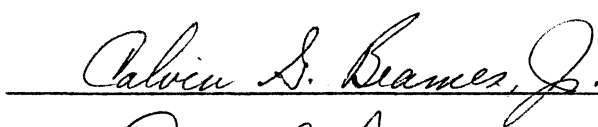
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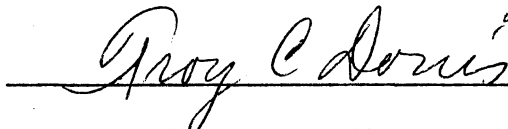
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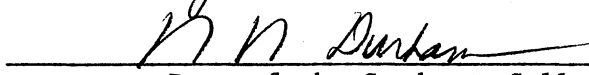
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## PREFACE

The objectives of this study were to (1) measure the concentrations of four heavy metals in the water, sediments, and chironomids in Skeleton Creek above and below the outfall of oil refinery and municipal sewage effluents; (2) estimate accumulation of heavy metals in sediments and chironomids above levels in water; (3) determine if cool and warm season conditions change the distribution of heavy metals in water, sediments, and chironomids; (4) determine the effect of high discharge on concentrations of metals in water and sediments; and (5) determine if oil refinery equipment cleaning increases the concentrations of metals in water and sediments.

Dr. Jerry L. Wilhm served as major adviser. Drs. Calvin G. Beames, Jr., Troy C. Dorris, and William A. Drew served on the advisory committee and criticized the manuscript. Dr. Sterling L. Burks provided advice and facilities for atomic absorption analyses. Dr. Ronald W. McNew provided considerable assistance with the statistical design and analysis. Mr. Tommy W. Conklin assisted in field collections and laboratory analyses. Thanks are given to all these people for their assistance.

Special gratitude is expressed to Barbara, my wife, for her support and assistance throughout my graduate program.

## TABLE OF CONTENTS

Chapter	Page
I. INTRODUCTION . . . . .	1
II. REVIEW OF RELATED LITERATURE . . . . .	4
III. DESCRIPTION OF SKELETON CREEK . . . . .	10
General Description . . . . .	10
Sources of Waste Effluents . . . . .	12
Sampling Stations . . . . .	13
IV. METHODS . . . . .	14
Sampling Regime . . . . .	14
Field Methods . . . . .	14
Laboratory Methods . . . . .	15
Statistical Methods . . . . .	19
V. PRECISION, ACCURACY, AND INTERFERENCES . . . . .	21
Precision and Accuracy of Atomic Absorption Analyses . . . . .	21
Interferences . . . . .	22
VI. WINTER - SUMMER SEASONS COMPARISONS . . . . .	29
Environmental Conditions . . . . .	29
Copper, Chromium, and Zinc in Water . . . . .	32
Copper, Chromium, Lead, and Zinc in Sediments . . . . .	41
Copper, Chromium, Lead, and Zinc in Chironomids . . . . .	67
VII. CONDITIONS FOLLOWING HIGH DISCHARGE . . . . .	71
Environmental Conditions . . . . .	71
Copper, Chromium, and Zinc in Water . . . . .	75
Copper, Chromium, Lead, and Zinc in Sediments . . . . .	82
VIII. CONDITIONS FOLLOWING REFINERY CLEANUP . . . . .	88
Environmental Conditions . . . . .	88
Copper, Chromium, Lead, and Zinc in Water . . . . .	90
Copper, Chromium, Lead, and Zinc in Sediments . . . . .	94
IX. SUMMARY . . . . .	100

Chapter	Page
LITERATURE CITED . . . . .	102
APPENDIX . . . . .	109

## LIST OF TABLES

Table	Page
I. Operating Conditions of Varian Techtron AA-5 and Perkin-Elmer HGA-70 for Metal Analyses . . . . .	17
II. Precision and Accuracy of Metal Determinations in Water Using the Heated Graphite Atomizer . . . . .	22
III. Precision and Accuracy of Metal Determinations in Water Using Flame Atomic Absorption . . . . .	23
IV. Comparisons of Metal Concentrations Determined by the Standard Additions Method and the Aqueous Standards Method for Water Samples Using the HGA . . . . .	24
V. Winter and Summer Water Temperatures (C) . . . . .	30
VI. Winter and Summer pH Values . . . . .	30
VII. Concentrations of Heavy Metals in Chironomids . . . . .	68
VIII. Mean Water Temperature, Dissolved Oxygen, and pH . . . . .	71
IX. Means and Standard Deviations of Copper, Chromium, Lead, and Zinc After October Flood, 1973 . . . . .	86
X. Means for Cores Containing Oily Materials . . . . .	87
XI. Mean Water Temperature, Dissolved Oxygen, and pH . . . . .	90
XII. Chromium, Copper, Lead, and Zinc in Water, Sediments, and Biota Reported in the Literature . . . . .	110
XIII. Means and Differences for Copper in Water by Station in Winter . . . . .	114
XIV. Means and Differences for Zinc in Water by Station in Winter . . . . .	114
XV. Means and Differences for Copper in Sediments by Station and Season . . . . .	115
XVI. Means and Differences for Percent Loss on Ignition in Sediments by Station and Season . . . . .	116

Table	Page
XVII. Means and Differences for <0.5 mm Fraction Particle Size of Sediments by Station and Season . . . . .	117
XVIII. Means and Differences for Chromium in Sediments by Station and Season . . . . .	118
XIX. Means and Differences for Lead in Sediments by Station and Season . . . . .	119
XX. Means and Differences for Zinc in Sediments by Station and Season . . . . .	120



## LIST OF FIGURES

Figure	Page
1. Skeleton Creek and Major Tributaries . . . . .	11
2. Percent Suppression or Enhancement of Copper Absorption Signals With Various Sodium Concentrations . . . . .	26
3. Percent Suppression or Enhancement of Zinc Absorption Signals With Various Sodium Concentrations . . . . .	26
4. Percent Suppression or Enhancement of Chromium Absorption Signals With Various Sodium Concentrations . . . . .	28
5. Percent Suppression or Enhancement of Lead Absorption Signals With Various Sodium Concentrations . . . . .	28
6. Mean Dissolved Oxygen Concentration $\pm$ Standard Deviations for Each Station in Winter and Summer Seasons . . . . .	31
7. Mean Alkalinity $\pm$ Standard Deviations for Each Station in Winter and Summer Seasons . . . . .	31
8. Mean Turbidity $\pm$ Standard Deviations for Each Station in Winter and Summer Seasons . . . . .	33
9. Mean Copper Concentration in Water $\pm$ Standard Deviations for Each Station in Winter and Summer Seasons . . . . .	33
10. Mean Chromium Concentration in Water $\pm$ Standard Deviations for Each Station in Winter and Summer Seasons . . . . .	36
11. Mean Zinc Concentration in Water $\pm$ Standard Deviations for Each Station in Winter and Summer Seasons . . . . .	39
12. Mean Copper Concentration in Sediments $\pm$ Standard Deviations for Each Station in Winter and Summer Seasons . .	42
13. Mean Percent Loss on Ignition $\pm$ Standard Deviations in Sediments for Each Station in Winter and Summer Seasons . . .	44
14. Regression of Copper on Percent Loss on Ignition in Sediments for Winter Data . . . . .	45

Figure	Page
15. Regression of Copper on Percent Loss on Ignition in Sediments for Summer Data . . . . .	45
16. Mean Percent of the <0.5 mm Fraction Particle Size $\pm$ Standard Deviations in Sediments for Each Station in Winter and Summer Seasons . . . . .	46
17. Mean Copper Concentration for Each Station of August Samples Extracted With 1 N Ammonium Acetate ( $\text{NH}_4\text{OAc}$ ) and 1 N Nitric Acid ( $\text{HNO}_3$ ) . . . . .	49
18. Mean Chromium Concentration in Sediments $\pm$ Standard Deviations for Each Station in Winter and Summer Seasons . . . . .	51
19. Regression of Chromium on Percent Loss on Ignition in Sediments for Winter Data . . . . .	53
20. Regression of Chromium on Percent Loss on Ignition in Sediments for Summer Data . . . . .	53
21. Mean Chromium Concentration for Each Station of August Samples Extracted With 1 N Ammonium Acetate ( $\text{NH}_4\text{OAc}$ ) and 1 N Nitric Acid ( $\text{HNO}_3$ ) . . . . .	55
22. Mean Lead Concentration in Sediments $\pm$ Standard Deviations for Each Station in Winter and Summer Seasons . . . . .	57
23. Regression of Lead on Percent Loss on Ignition in Sediments for Winter Data . . . . .	59
24. Regression of Lead on Percent Loss on Ignition in Sediments for Summer Data . . . . .	59
25. Mean Zinc Concentration in Sediments $\pm$ Standard Deviations for Each Station in Winter and Summer Seasons . . . . .	62
26. Regression of Zinc on Percent Loss on Ignition in Sediments for Winter Data . . . . .	63
27. Regression of Zinc on Percent Loss on Ignition in Sediments for Summer Data . . . . .	63
28. Mean Zinc Concentration for Each Station of August Samples Extracted With 1 N Ammonium Acetate ( $\text{NH}_4\text{OAc}$ ) and 1 N Nitric Acid ( $\text{HNO}_3$ ) . . . . .	66
29. Mean Alkalinity and Turbidity by Sampling Dates Following High Stream Discharge . . . . .	73

Figure	Page
30. Alkalinity and Turbidity Means for Days After High Stream Discharge Adjusted by Multiple Regression Analysis for Differences Between Stations and Among Sampling Periods . . .	73
31. Daily Precipitation Recorded at Enid, Oklahoma . . . . .	74
32. Mean Daily Discharge Recorded at Kilometer 76 . . . . .	74
33. Mean Copper Concentration for Each Group of Sampling Dates After Rains Adjusted by Multiple Regression Analysis for Differences Between Stations and Among Days Following High Discharge . . . . .	76
34. Mean Copper Concentration by Days After High Stream Discharge Adjusted by Multiple Regression Analysis for Differences Between Stations and Among Sampling Periods . . . . .	76
35. Mean Chromium Concentration for Each Group of Sampling Dates After Rains Adjusted by Multiple Regression Analysis for Differences Between Stations and Among Days Following High Discharge . . . . .	78
36. Mean Chromium Concentration by Days After High Stream Discharge Adjusted by Multiple Regression Analysis for Differences Between Stations and Among Sampling Periods . . . . .	78
37. Mean Zinc Concentration for Each Group of Sampling Dates After Rains Adjusted by Multiple Regression Analysis for Differences Between Stations and Among Days Following High Discharge . . . . .	79
38. Mean Zinc Concentration by Days After High Stream Discharge Adjusted by Multiple Regression Analysis for Differences Between Stations and Among Sampling Periods . . . . .	80
39. Means of Heavy Metal Concentrations and Percent Loss on Ignition by Sampling Periods After Rainfall Adjusted by Multiple Regression Analysis for Difference Between Stations and Among Days After High Stream Discharge . . . . .	83
40. Means of Heavy Metal Concentrations and Percent Loss on Ignition by Days After High Stream Discharge Adjusted by Multiple Regression Analysis for Differences Between Stations and Among Sampling Periods . . . . .	84
41. Mean Alkalinity and Turbidity by Sampling Dates Following Refinery Cleanup . . . . .	89

Figure	Page
42. Mean Copper Concentration in Water $\pm$ Standard Deviations for Sampling Dates Following Refinery Cleanup . . . . .	91
43. Mean Chromium Concentration in Water $\pm$ Standard Deviations for Sampling Dates Following Refinery Cleanup . . . . .	92
44. Mean Lead Concentration in Water $\pm$ Standard Deviations for Sampling Dates Following Refinery Cleanup . . . . .	93
45. Mean Zinc Concentration in Water $\pm$ Standard Deviations for Sampling Dates Following Refinery Cleanup . . . . .	95
46. Mean Copper Concentration in Sediments $\pm$ Standard Deviations for Sampling Dates Following Refinery Cleanup . . . . .	97
47. Mean Chromium Concentration in Sediments $\pm$ Standard Deviations for Sampling Dates Following Refinery Cleanup . . . . .	97
48. Mean Lead Concentration in Sediments $\pm$ Standard Deviations for Sampling Dates Following Refinery Cleanup . . . . .	98
49. Mean Zinc Concentration in Sediments $\pm$ Standard Deviations for Sampling Dates Following Refinery Cleanup . . . . .	99

## CHAPTER I

### INTRODUCTION

Heavy metals from industrial and municipal wastes have been accumulating in the sediments of lakes and streams (Anderson, Phillips, and Schriver 1971). Trace contaminants, including heavy metals, may have effects on the ecosystem as great or greater than the more common pollutants (Lucas, Edgington, and Colby 1970). Heavy metals in low concentrations result in abnormal and suppressed growth (Bowen 1966). Heavy metals are toxic at high concentrations (Doudoroff and Katz 1953). The "pollutional potential" of copper, chromium, lead and zinc has been rated as very high (Bowen 1966).

Heavy metals are unevenly distributed in aquatic ecosystems (Mathis and Cummings 1971, 1973) and tend to be associated with the suspended and colloidal material (Shapiro 1964; O'Connor and Renn 1964; Williams, Kopp, and Tarzwell 1966). Distribution of trace metals among sediments, water and biota of an estuary was influenced by the chemical and physical states of the metals and the estuary and the affinity of the metals for accumulation by biota and adsorption on particulate matter (Cross, Duke, and Willis 1970). Similar factors probably govern heavy metal distribution in a freshwater stream.

Considerable variation exists in the distribution of metals in freshwater ecosystems. Heavy metals generally exist in low levels in water and attain considerable concentration in sediments and biota

(Mathis and Cummings 1971, 1973; Oliver 1973). Illinois River sediments averaged 19  $\mu\text{g/g}$  copper in water containing only 1  $\mu\text{g/l}$  (Mathis and Cummings 1971). Lead accumulated from 2.1  $\mu\text{g/l}$  in water to 28  $\mu\text{g/g}$  in sediments. Chromium, nickel, and zinc were similarly concentrated in sediments. Aquatic organisms also accumulated metals. Tubificids contained 24  $\mu\text{g/g}$  copper, while non-carnivorous fish had 0.21  $\mu\text{g/g}$ . The American oyster had a concentration factor approaching 150,000 times for zinc (Pringle, Hissong, and Katz 1968). A freshwater dragonfly had a concentration factor of 20 for zinc (Kormondy 1965).

Municipal and industrial discharges and surface water runoff add significant amounts of trace metals to sediments of aquatic ecosystems (Shimp, Leland, and White 1970; Shimp et al. 1971). Surface layers of sediments had higher concentrations of heavy metals than deeper layers. Reductions of 140, 70, and 85  $\mu\text{g/g}$  for zinc, lead, and copper, respectively, have been measured in the first 6 cm of Southern Lake Michigan sediments. Other metals show similar trends.

Seasonal fluctuations of heavy metal concentrations in water may be concealed by irregular variations in municipal and industrial waste discharges (Chawla and Chau 1969). Monthly variations of manganese, iron, and zinc in the Newport River estuarine sediments were considerable but did not reveal a seasonal pattern (Cross et al. 1970). Confusion remains concerning the presence or absence of seasonal influence on the distribution and abundance of heavy metals in stream water and sediments.

Metals accumulated in sediments are removed from upstream areas during high discharge and deposited farther downstream (Williams et al. 1966, 1973). It is not known if metal concentrations of stream sediments

undergo net change following heavy rainfalls and a period of high stream discharge and scouring.

Heavy metals present in crude oils or added during the refining process accumulate on the refinery equipment (McCoy 1962). Refinery equipment is cleaned annually during the summer, and it is expected that this leads to a change in metal content of the oil refinery effluent.

The chemical or physical state of a heavy metal may make it unavailable for cycling within the ecosystem (Cross et al. 1970). A certain portion may be tightly bound to dissolved materials or sediments such that environmental changes in pH, dissolved oxygen, temperature, alkalinity, etc., are not sufficient for release. It is important, therefore, to consider the portion of these metals available for cycling within the system. Estimates of this fraction of metals have been made by measuring the acid-extractable fraction of metals in sediments and organic deposits (Nriagu 1967; Riemer and Toth 1970; John, Chuah, and VanLaerhoven 1972).

Skeleton Creek receives municipal and industrial wastes containing heavy metals and their salts. The objectives of this study were to (1) measure the concentrations of four heavy metals in water, sediments, and chironomids in Skeleton Creek; (2) estimate accumulation of the heavy metals in sediments and chironomids above levels in the water; (3) determine if cool and warm season conditions change the distribution of heavy metals in water, sediments, and chironomids; (4) determine the effect of high discharge on concentrations of metals in water and sediments; and (5) determine if oil refinery equipment cleaning increases the concentrations of metals in water and sediments.

## CHAPTER II

### REVIEW OF RELATED LITERATURE

Public concern over heavy metal contamination of lakes and streams has recently increased. One hundred ten people were severely disabled or died between 1953 and 1960 after eating fish and shellfish caught in Minamata Bay, Japan. The fish and shellfish were contaminated with mercury (Konrad 1971). The wide use of leaded gasoline has resulted in an alarming buildup of lead in ecosystem components such as stream bottom sediments, soils, and biota (Rolfe and Edgington 1973). Positive correlations exist between cardiovascular mortality and trace element concentrations in water supplies (Andelman 1973). Other metals may have similar but less dramatic effects as they too are accumulating in aquatic ecosystems.

Considerable variation in trace metals exists among streams and rivers in the United States (Table XII, Appendix). Durum, Hem, and Heidel (1971) found the highest concentration of zinc (42,000  $\mu\text{g/l}$ ) in Mineral Creek near Big Dome, Arizona; lead (890  $\mu\text{g/l}$ ) in the St. Croix River, Baring, Maine; and chromium (19  $\mu\text{g/l}$ ) in Irish Buffalo Creek near Concord, North Carolina. Kopp and Kroner (1968) found the highest concentration of zinc (1182  $\mu\text{g/l}$ ) in the Cuyahoga River at Cleveland, Ohio; lead (140  $\mu\text{g/l}$ ) in the Ohio River, Indiana; chromium (112  $\mu\text{g/l}$ ) in the St. Lawrence River, New York; and copper (280  $\mu\text{g/l}$ ) in the Monongahela River, Pennsylvania. The zinc concentration in the Arkansas River near



Ponca City, Oklahoma, was 19  $\mu\text{g/l}$  (Kopp and Kroner 1968). Lead and zinc concentrations in the Kiamichi River near Big Cedar, Oklahoma, were 84  $\mu\text{g/l}$  and 790  $\mu\text{g/l}$ , respectively (Durum et al. 1971). Maximum values reported for the lower North Canadian River waters were 550, 820, and 7200  $\mu\text{g/l}$  for copper, zinc, and chromium, respectively (Frank 1969). In contrast, Bradford, Bair, and Hunsaker (1968) reported low median concentrations of 15 elements in waters of 170 High Sierra lakes in California. For example, 1.5  $\mu\text{g/l}$  zinc, 1.2  $\mu\text{g/l}$  copper, and 0.5  $\mu\text{g/l}$  lead were reported. Chromium was detected in only two samples from the 170 lakes. Levels of 15  $\mu\text{g/l}$  copper, 8  $\mu\text{g/l}$  zinc, and 4  $\mu\text{g/l}$  lead have been reported for Lake Erie (Chawla and Chau 1969). Minnesota lakes are intermediate in trace metal concentrations when compared to the High Sierra lakes and Lake Erie (Bright 1968). The Minnesota lakes had levels of 5.2  $\mu\text{g/l}$  copper and 7.5  $\mu\text{g/l}$  zinc. Mean concentrations of trace metals in drinking waters in 37 locations in the United States were 136  $\mu\text{g/l}$  zinc, 11  $\mu\text{g/l}$  lead, and 59  $\mu\text{g/l}$  copper (Kohoe, Cholak, and Largent 1944). A recent survey of Wisconsin public drinking water supplies indicated low concentrations of heavy metals distributed throughout the state, but all water sources met the drinking water standards of the Public Health Service (Baumeister 1972). The Saale River, which flows through an industrialized region in Germany, had concentrations of 116 to 332  $\mu\text{g/l}$  zinc (Heide and Singer 1954). At one point this river receives wastes containing 3500  $\mu\text{g/l}$  zinc, but this is lost from solution shortly after the point of discharge.

Trace metals generally occur in lower concentrations in alkaline streams than in acidic waters. Huff (1948) reported a mean zinc concentration of 530  $\mu\text{g/l}$  in Colorado and Missouri streams receiving acid mine

drainage (pH 3). Observations as high as 98,000 and 60,000  $\mu\text{g}/\text{l}$  were reported. Zinc concentrations in rivers of the Chesapeake Bay region ranged from 12 to 580  $\mu\text{g}/\text{l}$  (O'Connor et al. 1964). The Chesapeake Bay tributaries having a pH range of 6.5 to 6.9 averaged 73  $\mu\text{g}/\text{l}$  zinc, those with a 7.0 to 7.4 range averaged 65  $\mu\text{g}/\text{l}$ , streams with a 7.5 to 7.9 range averaged 45  $\mu\text{g}/\text{l}$ , and those with a pH range of 8.0 to 8.3 averaged 26  $\mu\text{g}/\text{l}$ .

Sediments have a much higher heavy metal concentration than the overlying waters (Table XII, Appendix). Big Gunpowder Falls River, Maryland, had a zinc concentration of 116  $\mu\text{g}/\text{l}$  while the sediments contained 398  $\mu\text{g}/\text{g}$  (O'Connor et al. 1964). At one location on the Potomac River the water averaged 41  $\mu\text{g}/\text{l}$  zinc and the sediments averaged 400,000  $\mu\text{g}/\text{g}$ . At another location the water averaged 650  $\mu\text{g}/\text{l}$  and the sediments averaged 152,000  $\mu\text{g}/\text{g}$  zinc. Illinois River water contained 1  $\mu\text{g}/\text{l}$  copper and the sediments contained 19,000  $\mu\text{g}/\text{g}$  (Mathis and Cummings 1971, 1973). Other metal concentrations in water and sediments were lead, 2  $\mu\text{g}/\text{l}$  and 2,800  $\mu\text{g}/\text{g}$ ; chromium, 21  $\mu\text{g}/\text{l}$  and 17,000  $\mu\text{g}/\text{g}$ ; and zinc, 31  $\mu\text{g}/\text{l}$  and 81,000  $\mu\text{g}/\text{g}$ .

Sediments in marine waters have similar concentration factors (Table XII, Appendix). Goldberg (1957) reported a mean concentration of 3  $\mu\text{g}/\text{l}$  copper in marine waters, while the sediments of Tasman Bay, New Zealand, contained 102  $\mu\text{g}/\text{g}$  (Brooks and Rumsby 1965). The chromium level in Tasman Bay sediments was 307,000  $\mu\text{g}/\text{g}$  while seawater contained only 0.05  $\mu\text{g}/\text{l}$ . Copper also exhibited high levels of accumulation in the bay as the sediments contained 102,000  $\mu\text{g}/\text{g}$  while seawater contained 3  $\mu\text{g}/\text{l}$ . Iron concentration in seawater was 10  $\mu\text{g}/\text{l}$  with 73,000,000  $\mu\text{g}/\text{g}$  in the sediments (Brooks and Rumsby 1965). Iron in Lake Mendota,

Wisconsin, was 10  $\mu\text{g/l}$  while the sediment concentration reached 16,800  $\mu\text{g/g}$  (Nriagu 1967). Delfino et al. (1969) observed a comparable level of 26,700  $\mu\text{g/g}$  iron in Lake Mendota sediments. Using acid treated sample, Cross et al. (1970) estimated the concentration of zinc in the Newport River estuary as 6  $\mu\text{g/l}$  in water and 8,700  $\mu\text{g/g}$  in the sediments. Similarly, the iron concentration in water was 39  $\mu\text{g/l}$ , and 944,000  $\mu\text{g/g}$  in the sediments. Brunskill et al. (1971) estimated concentrations of chromium and zinc in the surface sediments of some Experimental Lakes, Canada, as 130 and 70  $\mu\text{g/g}$  ash weight, respectively. The metal concentrations of overlying waters were not estimated. Estimated concentrations of iron and magnesium in the surface sediments of the Experimental Lakes were 41,500 and 4,700  $\mu\text{g/g}$  ash weight, respectively (Brunskill et al. 1971). Mean concentrations of 50  $\mu\text{g/l}$  iron and 900  $\mu\text{g/l}$  magnesium were reported in the overlying waters (Armstrong and Schindler 1971).

Trace metals are positively correlated with percent organic carbon in the sediments. Working with Lake Michigan sediments, Shimp et al. (1971) reported that chromium had the best correlation with percent organic carbon throughout all sediment intervals. Copper, lead, and zinc also illustrated good correlations with organic carbon content. In one core, for example, the surface sediments had concentrations of 380,000  $\mu\text{g/g}$  zinc, 120,000  $\mu\text{g/g}$  chromium, and 3.58% organic carbon. At 6 cm in depth, the zinc decreased to 120,000  $\mu\text{g/g}$ , chromium to 60,000  $\mu\text{g/g}$ , and organic carbon to 1.82%. Correlation coefficients were greater with percent organic carbon than with sediment depth. Organic matter was found to adsorb more copper than three clays tested in a laboratory study (Riemer and Toth 1970). Gorham and Swaine (1965) reported that the relatively organic lake muds from the English Lake

District had the highest concentrations of carbon, copper, tin, and nickel. Although trace metal distribution was not measured, Waterville Lake, Tennessee, cores had a higher percentage of organic carbon in the upper 5 cm than at deeper levels (Ballinger and McKee 1971). In contrast, Bortleson (1971) reported that organic carbon concentration in the northern Wisconsin noncalcareous lakes increased with depth of sediment. Trace metals were negatively correlated with organic carbon content.

Heavy metals are generally found in higher concentrations in sediments composed of small particles compared to sediments with larger particle sizes (Oliver 1973). Average heavy metal concentrations of fine particle-size sediments (0.004 to 0.062 mm) were 33  $\mu\text{g/g}$  lead, 88  $\mu\text{g/g}$  zinc, 25  $\mu\text{g/g}$  copper, and 27  $\mu\text{g/g}$  chromium. Larger particle-sized sediments (0.5 to 2.0 mm) averaged 5  $\mu\text{g/g}$  lead, 24  $\mu\text{g/g}$  zinc, 9  $\mu\text{g/g}$  copper, and 9  $\mu\text{g/g}$  chromium. Higher metal concentrations in finer sediments are due to the larger adsorptive capacity associated with greater surface area (Oliver 1973).

Aquatic organisms accumulate metals to levels higher than those found in the water medium (Table XII, Appendix). Illinois River water contained 1, 2.9, and 2.1  $\mu\text{g/l}$  copper, nickel, and lead, respectively. Three species of clams from this river averaged 1.2 to 1.8  $\mu\text{g/g}$  copper, 1.1 to 2.1  $\mu\text{g/g}$  nickel, and 2.5 to 3.8  $\mu\text{g/g}$  lead (Mathis and Cummings 1971). These organisms had an increase in metal content of at least 1,000 fold when compared with the water concentrations. Two species of tubificids had even greater concentration factors. Zinc had a mean concentration of 40  $\mu\text{g/g}$  in the tubificids, while the water zinc level was 32  $\mu\text{g/l}$ . Similarly, copper in tubificids and water was 24  $\mu\text{g/g}$  and

1  $\mu\text{g}/\text{l}$ , respectively. Fish species from the Illinois River accumulated metals to a lesser degree than did the invertebrates. Non-carnivorous fish contained 0.21  $\mu\text{g}/\text{g}$  copper and 0.22  $\mu\text{g}/\text{g}$  chromium, while the river water had concentrations of 1  $\mu\text{g}/\text{l}$  copper and 210  $\mu\text{g}/\text{l}$  chromium. The American Eastern Oyster had concentrations of 1,428  $\mu\text{g}/\text{g}$  zinc and 91.5  $\mu\text{g}/\text{g}$  copper (Pringle et al. 1968). These concentrations represent concentration factors of 148,000 for zinc and 14,800 for copper. The dragonfly, Plathemis lydia, has been reported to have accumulated zinc approximately 20 times that of the water medium (Kormondy 1965). Spottail shiners from Lake Erie contained 1.2  $\mu\text{g}/\text{g}$  copper in whole fish (Lucas et al. 1970) from waters with a mean level of 15  $\mu\text{g}/\text{l}$  (Chawla and Chau 1969). Zooplankton collected from offshore Puerto Rico averaged 1,200  $\mu\text{g}/\text{g}$  iron and 426  $\mu\text{g}/\text{g}$  zinc (Martin 1970), while water concentrations had 10  $\mu\text{g}/\text{l}$  iron and 3  $\mu\text{g}/\text{l}$  zinc. Nickel content of marine crustaceans was 2  $\mu\text{g}/\text{g}$  compared with 1  $\mu\text{g}/\text{l}$  in the water (Fukai and Meinke 1959). Newport River estuarine polychaetes contained approximately 95  $\mu\text{g}/\text{g}$  zinc in water containing 0.6  $\mu\text{g}/\text{l}$  (Cross et al. 1970). Iron concentration in the water was 39  $\mu\text{g}/\text{l}$  compared with an accumulated 940  $\mu\text{g}/\text{g}$  in the polychaetes.

## CHAPTER III

### DESCRIPTION OF SKELETON CREEK

#### General Description

Skeleton Creek originates near Enid, Garfield County, Oklahoma, flows southeasterly for 113 km through Kingfisher and Logan Counties, and empties into the Cimarron River 8 km north of Guthrie (Figure 1). Stream elevation is 387 m at Enid and 227 m at the confluence with the Cimarron River. Mean gradient is 0.9 m/km. Width along most of the stream is 6 to 9 m and widens to 15 m near the mouth. Depth of water varies from a few centimeters in riffles to over 1.5 m in deeper pools. Low flow occurs throughout most of the year with a mean annual flow of  $1.4 \text{ m}^3/\text{sec}$  (Wilhm and Dorris 1966). Skeleton Creek passes from a third order stream at the uppermost station to a sixth order stream at the lowermost station (Horton 1945). The watershed area is approximately 106,230 ha (U. S. Department of Interior 1974). Over 80% is cultivated or open pasture (Soil Conservation Service 1958).

The drainage basin is located in Permian sandstones, clays, and shales (Galloway 1960). The heavy red shales underlying the upper basin belong to the Lower Enid Formation, commonly referred to as Permian Red Beds (Gray and Galloway 1959). Most soils of the area belong to the Renfrow-Zaneis-Vernon association. The surface soils are brown to reddish-brown clay, silt, or sandy loams weathered from red shales, sandstones, and clays (Gray and Galloway 1959).

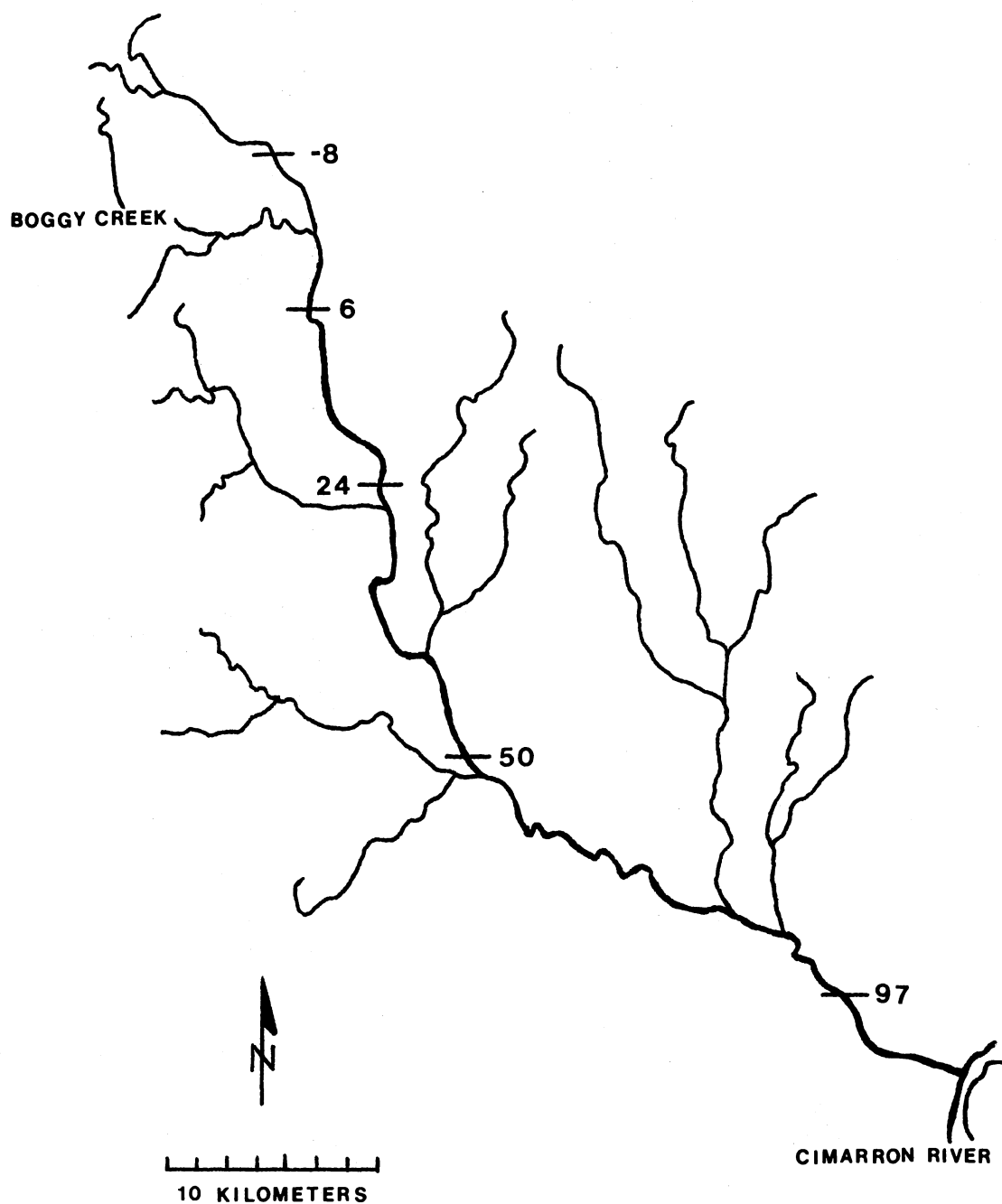


Figure 1. Skeleton Creek and Major Tributaries. Sampling Stations are Indicated by Distance in Kilometers Upstream (-) and Downstream ( ) From the Confluence of Boggy and Skeleton Creeks

Climate of the Skeleton Creek area is continental with wide seasonal temperature variations. Winters are mild with short cold periods. Summers are warm with the temperature often exceeding 40 C. Temperature ranged from -31 to 46 C and averaged 15 C for a 61-year period through 1953. Mean annual precipitation for this period was 76 cm. Driest months are from December through February (Galloway 1960). The frost-free season averages 215 days, from about March 30 to October 31 (Fitzpatrick, Boatright, and Rose 1939).

#### Sources of Waste Effluents

Municipal and industrial wastes from five sources enter the headwaters of Skeleton Creek. Approximately 400 m<sup>3</sup>/day of domestic sewage effluent from an aerated sewage lagoon in North Enid enter Skeleton Creek 10 km above its confluence with Boggy Creek. The Enid State School sewage effluent of 600 m<sup>3</sup>/day enters Skeleton Creek 3 km downstream from the sewage lagoons. The school treatment facilities consist of an Imhoff Tank, a trickling filter, and a final settling basin. Other wastes enter Skeleton Creek in the discharge of Boggy Creek.

Boggy Creek originates southwest of Enid and receives effluents from three sources. An Air Force Base releases effluents of domestic wastes. The waste treatment plant at the Air Force Base has a primary settling basin, trickling filter, sludge-drying beds, and a final settling basin. Mean outfall during the summer months of 1973 was approximately 720 m<sup>3</sup>/day. Boggy Creek receives the Enid municipal sewage effluent about 1.5 km above the confluence with Skeleton Creek. Treatment includes preaeration, activated sludge, and sludge drying. Approximately 18,550 m<sup>3</sup>/day of sewage are treated and over 80% of the



final effluent is pumped to an oil refinery for use in the refining process. The refinery effluent is passed through an API Trap for oil removal and pumped into a series of six settling pits where it is mixed with boiler blow-down and lime slurry. A series of five oxidation ponds then receives the waste water. A final effluent of 4,000 m<sup>3</sup>/day, including storm runoff, flows into Boggy Creek 90 m above the Enid sewage treatment plant outfall.

Oil wells are present in the basin area between 8 and 71 km from the confluence of Boggy Creek and Skeleton Creek.

#### Sampling Stations

Five stations were selected and numbered according to their distance in kilometers from the confluence of Boggy Creek with Skeleton Creek (Figure 1). The first station is upstream from the junction of the two streams and the remaining four are located below the confluence.

## CHAPTER IV

### METHODS

#### Sampling Regime

Samples were collected between February 10 and October 25, 1973. Samples for comparisons between cool and warm seasons were collected from five stations on two dates each in February and August. Stations 6 and 97 were sampled for comparisons among days following high stream discharge. Six sets of samples were collected two days after flooding subsided, while three, two, and one set were taken 4, 8, and 16 days, respectively, after flooding subsided. Sediment samples were collected at Stations 6 and 97 on October 19 and 25 after the Enid area received 40 cm of rainfall in 24 h. Stations 6 and 97 were sampled for comparisons before and after refinery cleanup. Collections were made 1 day before and 2, 4, 8, and 16 days following the date effluents from the refinery were expected to reach Skeleton Creek.

#### Field Methods

Water and sediment collections began at the downstream stations and concluded at the upstream station. Eight water samples were taken at each station at one-half the total water depth. Water samples were collected in acid-washed 250 ml polyethylene bottles. Five samples were acidified with 2 ml of concentrated nitric acid which kept the sample

below pH 2 and allowed storage without significantly altering the metal content of the water. The remaining three samples were returned to the laboratory for alkalinity and light transmission analyses. Twelve sediment samples from each station were collected along two transects across the stream with three sampling sites per transect. Six sediment samples were used for metal analyses and six duplicates were analyzed for particle size and organic matter. Each sediment sample consisted of a core 3 cm in diameter X 5 cm long. Core collections were made by forcing polyethylene golf bag tubes into the stream bed. The tube ends were sealed with rubber stoppers and were later frozen until analyses were made.

Duplicate chironomid samples of approximately 0.5 g wet weight each were collected with a dip net at Station 6 on August 23 and 25, 1973. Samples were kept frozen in polyethylene bottles until analyses were made. Dissolved oxygen was determined using the Alsterberg (Azide) Modification of the Winkler method (A.P.H.A. 1971). Phenolphthalein and methyl orange alkalinity was determined as described in Standard Methods (A.P.H.A. 1971). A Hellige comparator was used for the determination of hydrogen ion concentration. Water temperature was determined with a mercury centigrade thermometer. Daily precipitation data were obtained from Radio Station KCRC, Enid, Oklahoma, and represented rainfall on the upper water-shed only. Mean daily discharge was gauged at Kilometer 76 by the U. S. Geological Survey.

#### Laboratory Methods

Water samples were analyzed for the four heavy metals with a Perkin-Elmer HGA-70 heated graphite atomizer (HGA) coupled to a Varian

Techtron AA-5 atomic absorption spectrophotometer. The instruments were operated as recommended by the manufacturers' manuals (Table I). Each sample was injected three times into the carbon rod of the HGA with a 20  $\mu$ l Eppendorf micropipette. Sample atomization resulted in absorbance peaks which were recorded with a Bechman 10 in recorder. Corrections for background interferences were made with a hydrogen continuum spectrum lamp. Blanks containing only double deionized distilled water and 2 ml concentrated nitric acid were run to check for contamination from containers and reagents. Metal concentrations in the samples were determined by comparing corrected peak heights to standard curves prepared by analyzing standard aqueous solutions of known metal concentrations.

The method of standard additions was used to estimate matrix and chemical interferences (Ramirez-Munoz 1968). Several samples were spiked with microliter amounts of known concentrated stock solutions. Volume changes were less than 1% and volume corrections were unnecessary. Absorption values were determined for the samples and for three samples spiked with known quantities of the element in question. These values were plotted on a graph of absorbance vs. spike concentration. The leftward extension (negative) of the "spike concentration" axis was a reversed order designation of the concentration interval. Extrapolation of the plotted line to the left intercept gave the concentration of the metal in the original sample. These values were compared to the estimates of metal concentration obtained by comparisons with the standard curves.

The extraction procedure used was modified from those of Nriagu (1967), Riemer and Toth (1970), and John et al. (1972). Approximately

TABLE I  
OPERATING CONDITIONS OF VARIAN TECHTRON AA-5  
AND PERKIN-ELMER HGA-70 FOR METAL ANALYSES

Parameter	Cr	Cu	Pb	Zn
Wavelength (Å)	3578.7	3247.5	2170.0	2138.6
Monochromator slit width (μ)	100	100	300	100
Fuel <sup>a</sup>	nitrous oxide - acetylene	air- acetylene	air- acetylene	air- acetylene
Lamp (mA)	5	3	6	6
Drying temperature (C)	95	95	95	95
Drying time (sec)	40	40	40	40
Ashing temperature (C)	1000	1000	470	470
Ashing time (sec)	90	90	90	90
Atomization temperature (C)	2400	2400	2400	1800
Atomization time (sec)	20	20	20	20
Detection limit (μg/l)				
Flame AA	100	40	100	40
HGA	1	1	5	<1

a - used only for flame atomic absorption.

15 g of the top 5 cm of sediment from each frozen core was placed in a tared 200 ml polyethylene flask, dried in an oven at 105 C for 12 h, placed in a desiccator for at least 1 h, and reweighed to obtain the dry weight. Fifty ml 1 N nitric acid was added to each flask. The flasks were then shaken on an Eberbach shaker for 12 h. Chromium, copper, lead, and zinc concentrations in the extracts were determined by aspirating the liquid into the flame atomic absorption spectrophotometer. Aqueous standard solutions were aspirated, absorbance values recorded, and standard curves prepared. Corrected sample absorbance values were compared to the standard curves to obtain metal content of the liquid. The metal concentration of the sediment sample was calculated using the equation,

$$\frac{\text{metal in solution (mg/l)}}{\text{sample wt (g)}} \times \frac{50 \text{ ml}}{\text{sample wt (g)}} = \frac{\text{metal in sediment}}{\text{(}\mu\text{g/g)}}$$

The method of standard additions was used to estimate matrix and chemical interferences in the manner listed above.

An extraction technique modified slightly from that of Jackson (1958) was used for removing adsorbed metals from sediments. Approximately 6 to 8 g of dry sediment was extracted in 50 ml 1 N ammonium acetate (pH 7) by shaking on an Eberbach shaker for 12 h. After allowing suspended sediment to settle, the samples were decanted. The supernatant was acidified to pH 2 with concentrated nitric acid and stored. Zinc concentrations were determined with flame atomic absorption while copper, chromium, and lead were measured with the HGA.

The replicate frozen sediment cores were analyzed for particle size distribution and organic matter content. The top 5 cm from each core was placed in a 200 ml polyethylene flask and oven dried for 12 h at 105 C. The samples were passed through a vertical nest of five sieves with

openings ranging from 0.5 to 5.0 mm (Welch 1948). The dry weight of each particle size range was recorded.

Approximately 10 g dry weight sediment from each core was placed in tared Coors porcelain crucibles, dried at 105 C for 12 h, reweighed, ignited at 500 C for 12 h, and reweighed to obtain loss on ignition (Schnitzer, Wright, and Hoffman 1959).

Frozen chironomid samples were placed in tared Vitreosil quartz crucibles, dried for 12 h at 105 C, reweighed to obtain dry weight, and ashed in a muffle furnace for 12 h at 500 C. The ash was dissolved by adding 10 ml 0.1 N hydrochloric acid to the crucibles. Samples were transferred to acid-washed polyethylene bottles. The crucibles were rinsed with double deionized distilled water and the volume was brought to 25 ml. Chromium, copper, and lead were analyzed by sample injections into the HGA-70, and zinc was analyzed by aspirating samples into the flame atomic absorption spectrophotometer. The metal concentrations of the chironomids were determined by the equation,

$$\frac{\text{metal in solution}}{(\text{mg/l})} \times \frac{25 \text{ ml}}{\text{chironomid wt (g)}} = \frac{\text{metal in chironomid}}{(\mu\text{g/g})}$$

#### Statistical Methods

Statistical analyses were performed on an IBM 360 computer using the Statistical Analysis Systems (SAS) Program. Comparisons of metal concentrations and physicochemical parameters between cool and warm seasons and among the five sampling stations were made with an analysis of variance (AOV). An AOV was also used for comparisons between stations and among sampling dates before and after the oil refinery clean-up. Protected Least Significant Difference (LSD) tests (Steele and

Torrie 1960) were used to detect significant differences among pairs of means. Simple linear regression lines were determined by the least squared method and used in studying relationships between metal concentrations and percent loss on ignition and between metal concentrations and distances downstream from waste effluents. Student's t-tests were conducted to determine if regression coefficients were significantly different from zero. Multiple regression analyses were used to adjust the means of metal concentrations and physicochemical factors for differences in sampling dates, stations, and days following high stream discharge. This method was used instead of the AOV because the 2, 4, 8, and 16 day categories were not sampled equally. In all statistical analyses values below the detection limit were treated as zeros.



## CHAPTER V

### PRECISION, ACCURACY, AND INTERFERENCES

#### Precision and Accuracy of Atomic Absorption Analyses

Precision and accuracy of determining heavy metal concentrations by atomic absorption were made by comparison with reference samples supplied by the Analytical Quality Control Laboratory, Cincinnati, Ohio. Reference samples were measured periodically during routine sample analyses. Precision of measuring metal concentrations was estimated by calculating a coefficient of variation for each metal by the formula,

$$\text{coefficient of variation (\%)} = \frac{100 \times \text{standard deviation } (\mu\text{g/l})}{\text{reference sample concentration } (\mu\text{g/l})}$$

Since the true means of reference samples were known, the standard deviations were determined by the formula:

$$\sqrt{\frac{(O - A)^2}{N}}$$

where O represents the observed concentration, A is the actual concentration of the reference sample, and N is the number of observations.

Accuracy was determined by calculating the average concentration by which the true concentration of the reference sample was over- or underestimated.

Heated graphite atomizer (HGA) analyses overestimated the concentrations of copper, chromium, and zinc in water (Table II). Lowest

variation and the highest error were for chromium determinations. Few analyses of reference samples and low metal concentrations contributed to the high percent errors.

TABLE II  
PRECISION AND ACCURACY OF METAL DETERMINATIONS  
IN WATER USING THE HEATED GRAPHITE ATOMIZER

Metal	Conc. ( $\mu\text{g}/\text{l}$ )	Number	Average Miss ( $\mu\text{g}/\text{l}$ )	Coeff. of Var. (%)	Error (%)
Copper	6.2	6	+1	21.0	16.1
Chromium	7.4	6	+1.3	19.1	17.6
Zinc	7.2	6	+1.2	22.2	16.7

(+) indicates values overestimated.

Metal concentrations determined by flame atomic absorption were measured with more precision and accuracy than those measured with the HGA. Copper was measured with the greatest precision while chromium measurements had the largest variability (Table III).

#### Interferences

Matrix interferences in metal determinations were estimated in Skeleton Creek water and sediment extracts by comparing metal concentrations measured by the standard additions method (Ramirez-Munoz 1968) with aqueous standards. Interference suppressed the absorption signal

in only one of five copper samples analyzed by the HGA (Table IV). Two of five chromium analyses had signal enhancement and one had signal suppression. Large interferences were found for zinc as four analyses had at least 50% signal suppression. These data indicated that zinc concentrations in Skeleton Creek water may have been nearly twice as high as reported in this study because no compensation was made for interference.

TABLE III  
PRECISION AND ACCURACY OF METAL DETERMINATIONS  
IN WATER USING FLAME ATOMIC ABSORPTION

	Conc. ( $\mu\text{g/l}$ )	Number	Average Miss ( $\mu\text{g/l}$ )	Coeff. of Var. (%)	Error (%)
Copper	208	10	-11	6.2	5.2
Chromium	185	11	-30	26.0	15.0
Lead	470	17	-65	16.2	13.0
Zinc	143	10	-4	11.1	2.9

(-) indicates values underestimated.

Copper, lead, and zinc concentrations in sediment extracts were also underestimated because of matrix interferences during flame atomic absorption analyses. Copper was underestimated by an average of 40  $\mu\text{g/l}$  in the 16 samples analyzed. Fifteen lead analyses resulted in a mean underestimation of 180  $\mu\text{g/l}$ , and zinc was underestimated by 870  $\mu\text{g/l}$  in

TABLE IV  
COMPARISONS OF METAL CONCENTRATIONS DETERMINED  
BY THE STANDARD ADDITIONS METHOD AND  
THE AQUEOUS STANDARDS METHOD FOR  
WATER SAMPLES USING THE HGA

Metal	Sample Number	Standard Additions ( $\mu\text{g/l}$ )	Aqueous Standards ( $\mu\text{g/l}$ )	% Suppression(-) or Enhancement(+)
Cu	8-23-1-1	6.0	6.0	0
	8-23-2-1	6.0	6.0	0
	8-23-3-1	7.5	7.5	0
	8-23-4-1	8.0	7.0	-12.5
	6-26-1-1	7.0	7.0	0
Cr	8-23-1-1	1.7	1.7	0
	8-23-2-1	1.5	1.7	-11.8
	8-23-3-1	4.0	4.0	0
	8-23-4-1	3.5	3.8	+7.9
	6-26-1-1	2.0	1.7	-15.0
Zn	8-23-0-1	2.0	1.0	-50.0
	8-23-1-1	2.0	2.0	0
	8-23-2-1	4.5	2.0	-55.6
	8-23-3-1	6.0	3.0	-50.0
	8-23-4-1	8.0	3.0	-62.5

20 analyses. In contrast, chromium was overestimated by an average of 30  $\mu\text{g/l}$  in 16 analyses.

Interferences in atomic absorption spectrophotometry are inaccuracies caused by chemical or physical properties of the sample interfering with metal absorption (Kahn 1968). Few investigators have studied interferences in samples from natural waters or sediment extracts. Fernandez and Manning (1971) using the HGA found matrix interferences for chromium and lead determinations in natural water samples. Several laboratories reported a wide range of values for reference samples with equal metal concentrations (Barnard and Fishman 1973). Matrix interferences were reported for copper, lead, and chromium. Zinc was not evaluated.

The physical and chemical properties of water are altered by various concentrations of sodium. Lead absorption signals were reduced by 30% when the sodium chloride level reached 300  $\mu\text{g/l}$  (Fernandez and Manning 1971). Extractions from Skeleton Creek sediments having higher sodium concentrations generally had a greater suppression of copper and zinc absorption signals (Figures 2 and 3). The relationships between suppression or enhancement of the absorption signal and sodium concentrations are expressed by the regression equations:

$$Y = 1.3311 + 0.0106 X \text{ for copper, and}$$

$$Y = 4.0687 + 0.0199 X \text{ for zinc.}$$

Regression coefficients were significantly different from zero ( $0.01 < p < 0.02$  for copper, and  $0.001 < p < 0.01$  for zinc). Because of solutes other than sodium, the lowest sodium concentrations did not always have the lowest interference. Regression coefficients of the relationships between sodium with chromium and lead were not significantly different

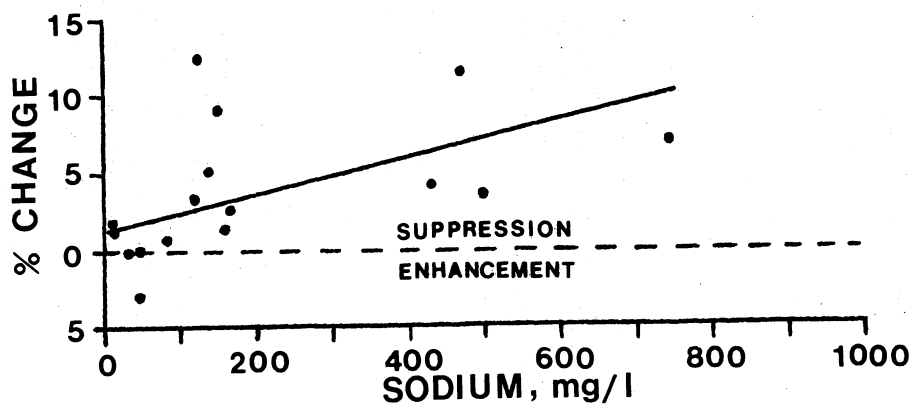


Figure 2. Percent Suppression or Enhancement of Copper Absorption Signals With Various Sodium Concentrations

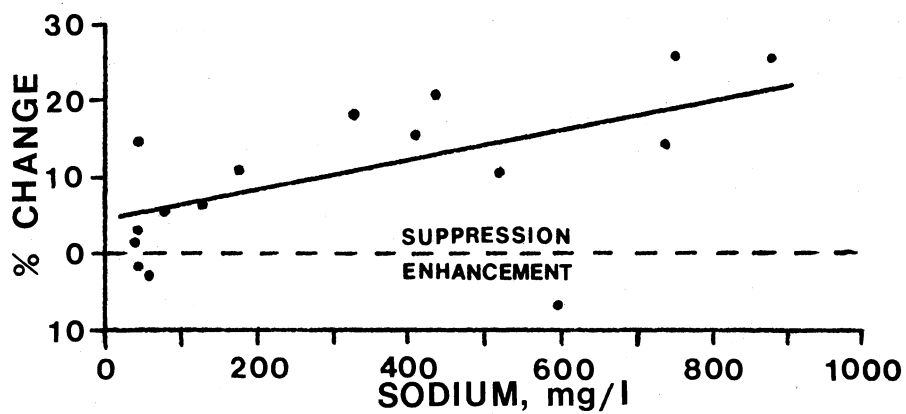


Figure 3. Percent Suppression or Enhancement of Zinc Absorption Signals With Various Sodium Concentrations

from zero (Figures 4 and 5). Solutes other than sodium apparently had a greater influence on interferences in determining these metals.

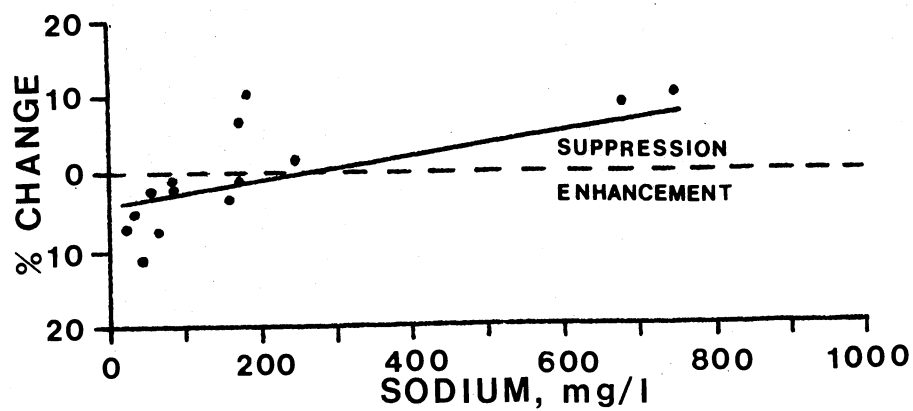


Figure 4. Percent Suppression or Enhancement of Chromium Absorption Signals With Various Sodium Concentrations

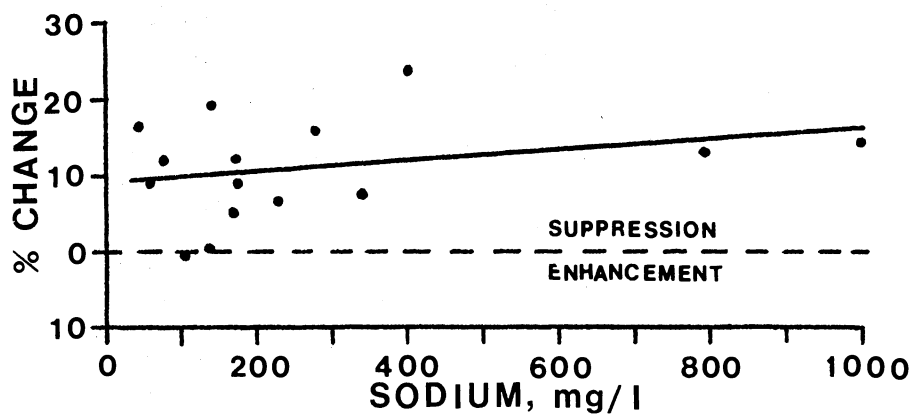


Figure 5. Percent Suppression or Enhancement of Lead Absorption Signals With Various Sodium Concentrations



## CHAPTER VI

### WINTER - SUMMER SEASONS COMPARISONS

#### Environmental Conditions

Temporal variation in water temperature exceeded spatial variation (Table V). Temperature ranged from 1 to 12 C on the winter sampling days and from 25 to 29 C on the summer days. Spatial variation was attributed to stream shading, depth, and station sampling order.

The concentration of dissolved oxygen in winter generally exceeded that in summer (Figure 6). Dissolved oxygen was greater at the upstream station than at the four downstream stations in winter. Station -8 was above the major sources of organic pollution and little deoxygenation by bacterial decomposition occurred. In summer, maximum dissolved oxygen occurred at Station 6 where high bacterial decomposition and deoxygenation was accompanied by dense algal growths.

Values of pH were generally higher at Station 97 than at the other stations (Table VI). Winter pH values exceeded summer values.

Although variation in methyl orange alkalinity between seasons was slight, considerable spatial variation existed (Figure 7). The maximum alkalinity at Station -8 was followed by a sharp decrease at Stations 6 and 24. This decrease was attributed to the oxidation of carbonaceous material to acids, microorganismal uptake of ammonia and its oxidation to nitric acid, and use of carbon dioxide and conversion of bicarbonates

TABLE V  
WINTER AND SUMMER WATER TEMPERATURES (C)

Dates	Stations				
	-8	6	24	50	97
10 Feb 73	7.0	8.0	3.0	2.0	1.0
27 Feb 73	12.0	12.0	7.0	6.0	6.0
23 Aug 73	29.0	27.0	26.0	26.0	27.0
25 Aug 73	27.0	28.0	25.0	26.0	27.0

TABLE VI  
WINTER AND SUMMER pH VALUES

Dates	Stations				
	-8	6	24	50	97
10 Feb 73	8.2	8.2	8.3	8.3	8.3
27 Feb 73	8.4	8.4	8.3	8.3	8.4
23 Aug 73	8.4	8.4	8.3	8.4	8.5
25 Aug 73	8.4	8.4	8.4	8.4	8.5

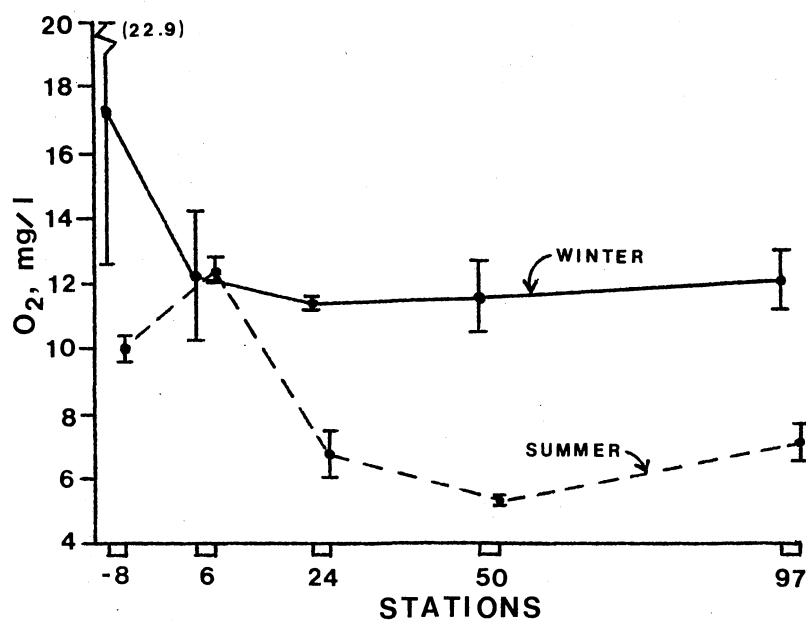


Figure 6. Mean Dissolved Oxygen Concentration  $\pm$  Standard Deviations for Each Station in Winter and Summer Seasons

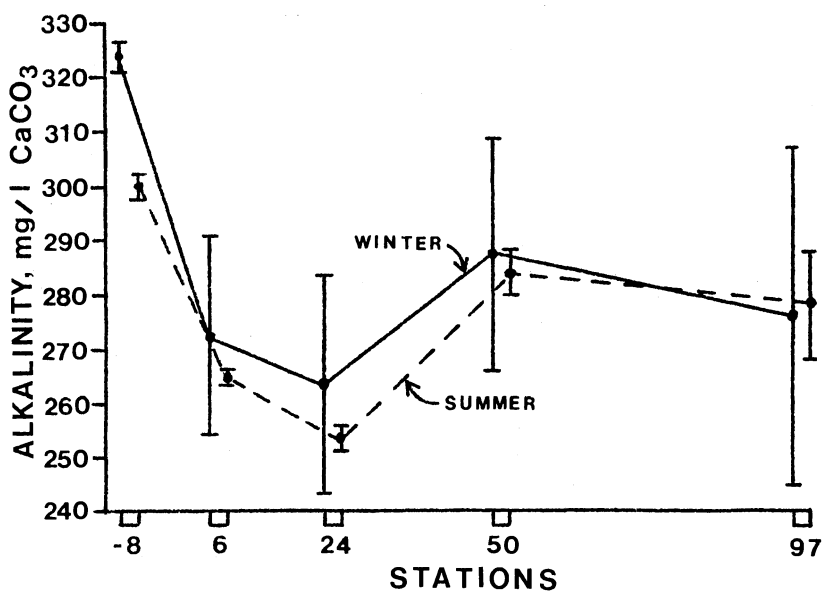


Figure 7. Mean Alkalinity  $\pm$  Standard Deviations for Each Station in Winter and Summer Seasons

to carbonates by algae (Klein 1957).

Turbidity increased abruptly with distance downstream from 18.5 Jackson Turbidity Units (JTU) at Station -8 to 88.0 JTU at Station 97 in winter and from 11.5 to 75.0 JTU in summer (Figure 8). Increased turbidity downstream was due to land erosion, inflow from tributaries, and resuspension of silt from the stream bed at higher discharges (Baumgardner 1966).

#### Copper, Chromium, and Zinc in Water

Skeleton Creek copper concentration averaged 4.1  $\mu\text{g/l}$ . This value was considerably smaller than the mean of 19.0  $\mu\text{g/l}$  for samples from the Southwest - Lower Mississippi River Basin (Kopp and Kroner 1968), but larger than the mean of 1  $\mu\text{g/l}$  in the Illinois River (Mathis and Cummings 1973). Higher values have been reported in other Oklahoma waters. Means were 22.0 and 6.5  $\mu\text{g/l}$  in the North Canadian River near Harrah and the Kiamichi River near Big Cedar, respectively (U. S. Department of Interior 1974).

Although copper concentrations in Skeleton Creek water were higher in winter samples than in summer (Figure 9), the difference between seasons was not significant ( $0.10 < p < 0.25$ ) because of the large variability among the few replicates. Significant difference was expected because the Enid refinery effluents generally contain more heavy metals in winter than in summer (Dr. Sterling Burks, Oklahoma State University, personal communication). In both seasons the minimum concentration occurred at Station -8 and the maximum at Station 6. Copper varied from 2.9 to 13.9  $\mu\text{g/l}$  in winter and from 0.3 to 3.5  $\mu\text{g/l}$  in summer. The Protected Least Significant Difference (LSD) test (Steele

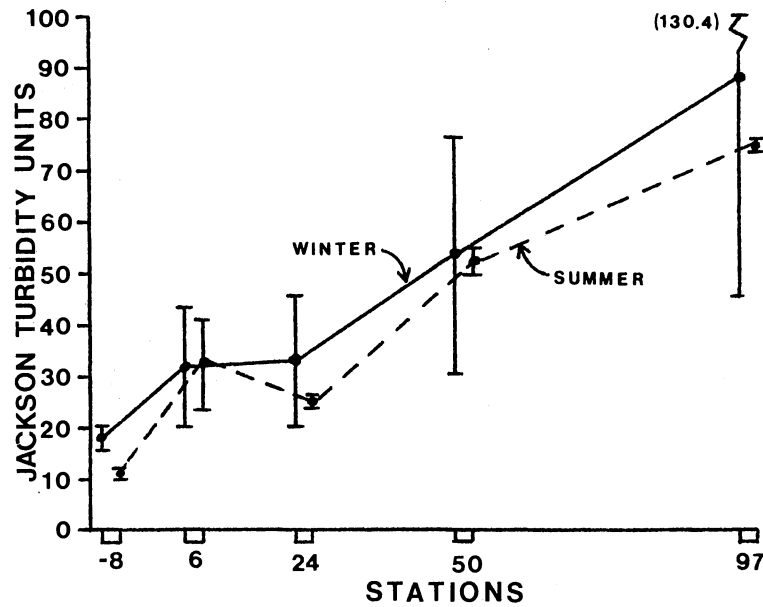


Figure 8. Mean Turbidity  $\pm$  Standard Deviations for Each Station in Winter and Summer Seasons

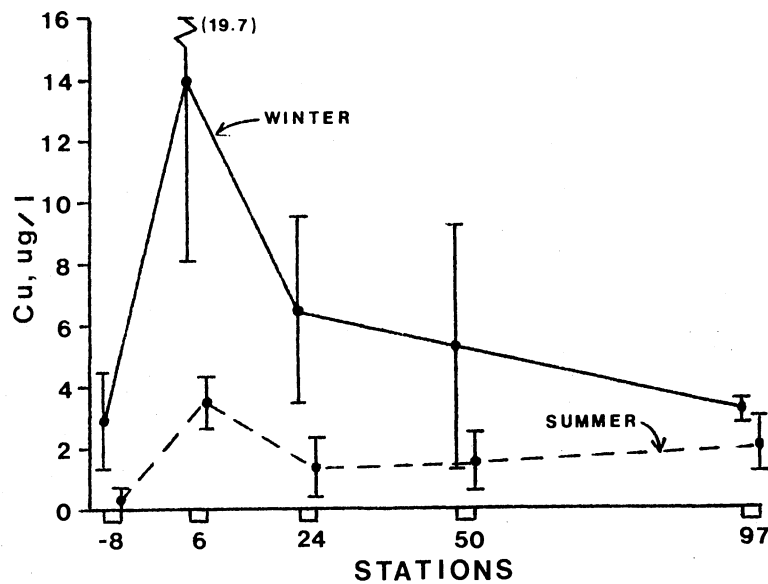


Figure 9. Mean Copper Concentration in Water  $\pm$  Standard Deviations for Each Station in Winter and Summer Seasons

and Torrie 1960) showed that Station 6 was significantly different from other stations in winter and no stations had significant differences in summer (Table XIII, Appendix).

The relationship of winter copper concentrations (Y) to distance downstream (X) from the confluence of Boggy and Skeleton Creeks was described by the following linear and logarithmic regression equations:

$$Y = 11.6042 - 0.0990 X, \text{ and}$$

$$\log Y = 1.0129 - 0.0058 X$$

Both equations were highly significant ( $p < 0.001$ ). Summer data did not significantly fit a logarithmic equation but the following linear equation was significant ( $0.02 < p < 0.05$ ):

$$Y = 2.7477 - 0.0113 X$$

Seasonal variation in copper concentration has been reported in other studies. Values in the Columbia River averaged 11.2 and 1.8  $\mu\text{g}/\text{l}$  in February and August, respectively (Silker 1964). A similar reduction occurred in the North Canadian River water but at higher concentrations (Frank 1969). February and August copper means were 111 and 92  $\mu\text{g}/\text{l}$ , respectively. These correspond to the trend observed in Skeleton Creek. In contrast, copper was higher in Illinois River water in August than in February. Mean values were 0.75 and 0.25  $\mu\text{g}/\text{l}$ , respectively. Reasons for contrasting data are unknown; however, seasonal variation of copper in the Columbia River reflected variation of flow from the major tributary streams. Copper concentration in the North Canadian River varied due to variation in discharge quantities of industrial and domestic wastes.

The reduction in copper concentration at downstream stations as observed in Skeleton Creek was observed in the Bee Fork Creek, Missouri

(Gale et al. 1973). However, the five stations sampled by Mathis and Cummings (1971) in the Illinois River did not differ in copper concentration. More variation might be expected because stations sampled were in areas above and below the city of Peoria. Similarly, little spatial variation existed in the Columbia River (Silker 1964). The Black Warrior River, Alabama, had little spatial variation at three successive downstream stations even though industrial effluents entering the river had a copper concentration in the 100 to 1,000  $\mu\text{g/l}$  range (Williams et al. 1973). Downstream stations had a 0.3 to 1.0  $\mu\text{g/l}$  range. Factors that influence spatial distribution of several heavy metals include ground water lithology, discharge from tributary streams, industrial effluents, and biological and inorganic processes (Andelman 1973). These factors probably influenced heavy metal distribution in Skeleton Creek.

Mean chromium concentration in Skeleton Creek was 1.1  $\mu\text{g/l}$ . Considerably higher levels of 16  $\mu\text{g/l}$  (Kopp and Kroner 1968) and 21  $\mu\text{g/l}$  (Mathis and Cummings 1973) were reported for the Southwest - Lower Mississippi River Basin and the Illinois River, respectively. Oklahoma streams also had higher chromium levels. Mean dissolved chromium was 8.5  $\mu\text{g/l}$  in the North Canadian River near Harrah and 5  $\mu\text{g/l}$  in the Kiamichi River near Big Cedar (U. S. Department of Interior 1974).

Seasonal and spatial variations in chromium concentration were small in Skeleton Creek (Figure 10). Because differences between season means and among station means were not significant, the LSD test was not used. Winter means increased from no detection at Station -8 to 3  $\mu\text{g/l}$  at Station 24, while summer means were all 1  $\mu\text{g/l}$ , or less.

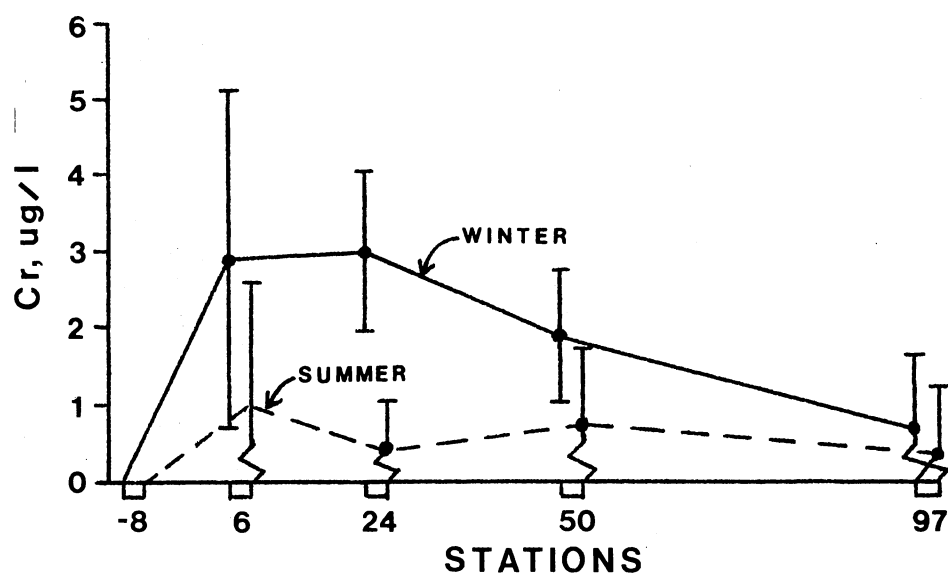


Figure 10. Mean Chromium Concentration in Water  $\pm$  Standard Deviations for Each Station in Winter and Summer Seasons



Winter chromium concentration (Y) decreased linearly with distance downstream (X) from the confluence of Boggy and Skeleton Creeks. The following linear regression equation for the winter data was significant ( $0.02 < p < 0.05$ ):

$$Y = 3.2838 - 0.0198 X$$

Winter data did not fit the logarithmic equation, and neither the linear nor the logarithmic equations fit the summer data significantly.

Considerable seasonal variation existed in chromium content of the Illinois River. The February mean of 43  $\mu\text{g/l}$  was reduced to 19  $\mu\text{g/l}$  in August (Mathis and Cummings 1971). The North Canadian River mean of 12.5  $\mu\text{g/l}$  in February was reduced to non-detectable levels in August. Comparable reductions of chromium were not observed in Skeleton Creek, possibly because chromium existed in low levels in the oil refinery effluents.

Spatial variation was slight in the Illinois River (Mathis and Cummings 1971), North Canadian River (Frank 1969), and Black Warrior River (Williams et al. 1973) as was the spatial variation in Skeleton Creek. Higher variation was expected in these streams because they received industrial and domestic wastes.

The mean concentration of zinc in Skeleton Creek of 9.9  $\mu\text{g/l}$  is much lower than the 85  $\mu\text{g/l}$  mean for the Southwest - Lower Mississippi River Basin (Kopp and Kroner 1968) and the 31  $\mu\text{g/l}$  Illinois River mean (Mathis and Cummings 1973). Two Oklahoma streams had more zinc than Skeleton Creek. Mean dissolved zinc was 35.4  $\mu\text{g/l}$  in the North Canadian River near Harrah, Oklahoma, and 188.2  $\mu\text{g/l}$  in the Kiamichi River near Big Cedar (U. S. Department of Interior 1974). The latter mean was high because 730  $\mu\text{g/l}$  zinc was recorded on one date.

Zinc concentration in Skeleton Creek water was much higher in winter than in summer (Figure 11). Difference between season means was significant at the 0.08 level. The Protected LSD test showed that Stations 6 and 24 were not significantly different from each other, but had significant differences from other stations in winter (Table XIV, Appendix). No stations had significant differences in summer. Minimum and maximum zinc concentrations occurred at Stations -8 and 6, respectively. Zinc concentration in winter increased abruptly from 6.7  $\mu\text{g/l}$  at Station -8 to 31.1  $\mu\text{g/l}$  at Station 6 and from an undetectable amount to 3.6  $\mu\text{g/l}$ , respectively, in summer. The high zinc level at Station 6 was the result of input of industrial and municipal waste effluents.

Linear and logarithmic regression equations were highly significant ( $p < 0.001$ ) in describing the relationship of zinc concentration (Y) with distance downstream (X) from the confluence of Boggy and Skeleton Creeks in both winter and summer. The winter regression equations were:

$$Y = 31.6830 - 0.2431 X, \text{ and}$$

$$\log Y = 1.5798 - 0.0093 X$$

Summer regression equations were:

$$Y = 3.2111 - 0.0242 X, \text{ and}$$

$$\log Y = 0.4991 - 0.0052 X$$

Seasonal variation in zinc concentration reported in other studies indicated no general trend. Illinois River zinc means were 54 and 13  $\mu\text{g/l}$  for February and August, respectively (Mathis and Cummings 1971). This trend corresponds to that observed in Skeleton Creek. Although seasonal variation was not discussed by Mathis and Cummings, the variation may be explained by industrial effluents entering the Illinois River since it receives wastes from several industries. The February

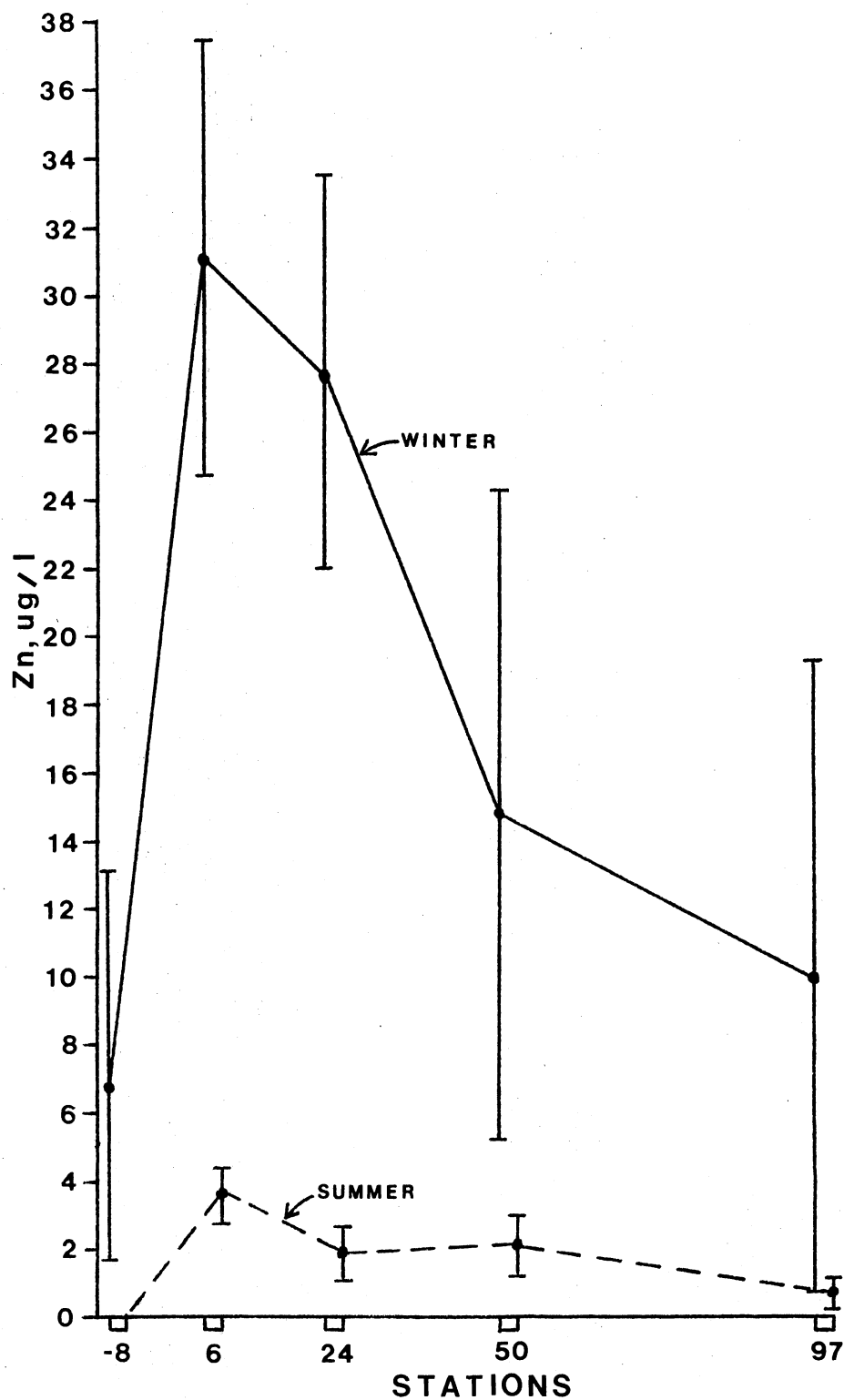


Figure 11. Mean Zinc Concentration in Water  $\pm$  Standard Deviations for Each Station in Winter and Summer Seasons

zinc mean of 5.6  $\mu\text{g/l}$  in the Columbia River was lower than the 16.8  $\mu\text{g/l}$  August mean (Silker 1964). A direct relationship was present between zinc concentration and Columbia River flow and seasonal variation was probably due to surface and ground water lithology. Cross et al. (1970) reported no seasonal trend in monthly variation of zinc in Newport River Estuary water. Monthly variation was not explained by Cross et al. but the influencing factors were noted to have affected the zinc concentrations in a similar manner at the three stations. Nearly equal February and August zinc means were found for the North Canadian River (Frank 1969). The February and August means were 91 and 98  $\mu\text{g/l}$ , respectively. Because the North Canadian River received large volumes of industrial and domestic waste effluents, the river probably was influenced greater by effluents than by seasonal environmental factors.

Spatial variations are undoubtedly influenced by domestic and industrial inputs. A pattern of spatial variation similar to that of Skeleton Creek was observed in Bee Fork Creek, Missouri (Gale et al. 1973). In both streams the station above the outfall had minimum concentrations and the first station below the pollution source had maximum levels. The downstream stations had lower zinc means. Similarly, the upstream station in the Illinois River had a much higher mean than the four downstream stations which were similar to each other (Mathis and Cummings 1971). Little variation existed among the downstream stations in the Illinois River. Spatial variation in zinc was minimal at the three stations in the Newport River Estuary (Cross et al. 1970). Similarly, no spatial variation was noted in the Black Warrior River, Alabama (Williams et al. 1973). The Newport River Estuary and Black Warrior River did not have major zinc inputs among the study areas.

Copper, Chromium, Lead, and Zinc  
in Sediments

The mean copper concentration in the sediments of Skeleton Creek was 1.8  $\mu\text{g/g}$ , which is considerably less than comparable values reported in the literature. Illinois River sediments had a mean copper concentration of 19  $\mu\text{g/g}$  (Mathis and Cummings 1973) and Mississippi River sediments averaged 10  $\mu\text{g/g}$  (Morris et al. 1972). Mean copper concentrations in the Ottawa and Rideau Rivers, Canada, were 28 and 24  $\mu\text{g/g}$ , respectively (Oliver 1973). The mean in the Potomac River Estuary was much higher than in Skeleton Creek (Pheiffer 1972). Namminga, Scott, and Burks (1974) and Sias (1974) reported 11.8 and 51.4  $\mu\text{g/g}$ , respectively, in Oklahoma lentic water sediments. Sediments from Upper Peoria Lake, a slow-flowing portion of the Illinois River, had a range of means for copper from 25 to 90  $\mu\text{g/g}$  (Collinson and Shimp 1972). Copper concentration in Skeleton Creek sediments may be low because of high stream discharge and scouring of the stream bed prior to sampling.

Copper concentration measured in summer was higher than that in winter (Figure 12). This difference was significant at the 0.09 level. Smaller significance levels were not present because of large variability among the few replicates. Maximum copper concentration occurred at Station 50 in both seasons, while the minimum level occurred at Station 6 in winter and Station -8 in summer. Differences in means among the five areas in Skeleton Creek were highly significant ( $p < 0.0005$ ). Winter copper means ranged from 0.3 to 1.9  $\mu\text{g/g}$  and summer levels were from 1.3 to 6.4  $\mu\text{g/g}$ . The Protected LSD test showed that Stations 24 and 50 were significantly different from Stations 6 and -8 in winter

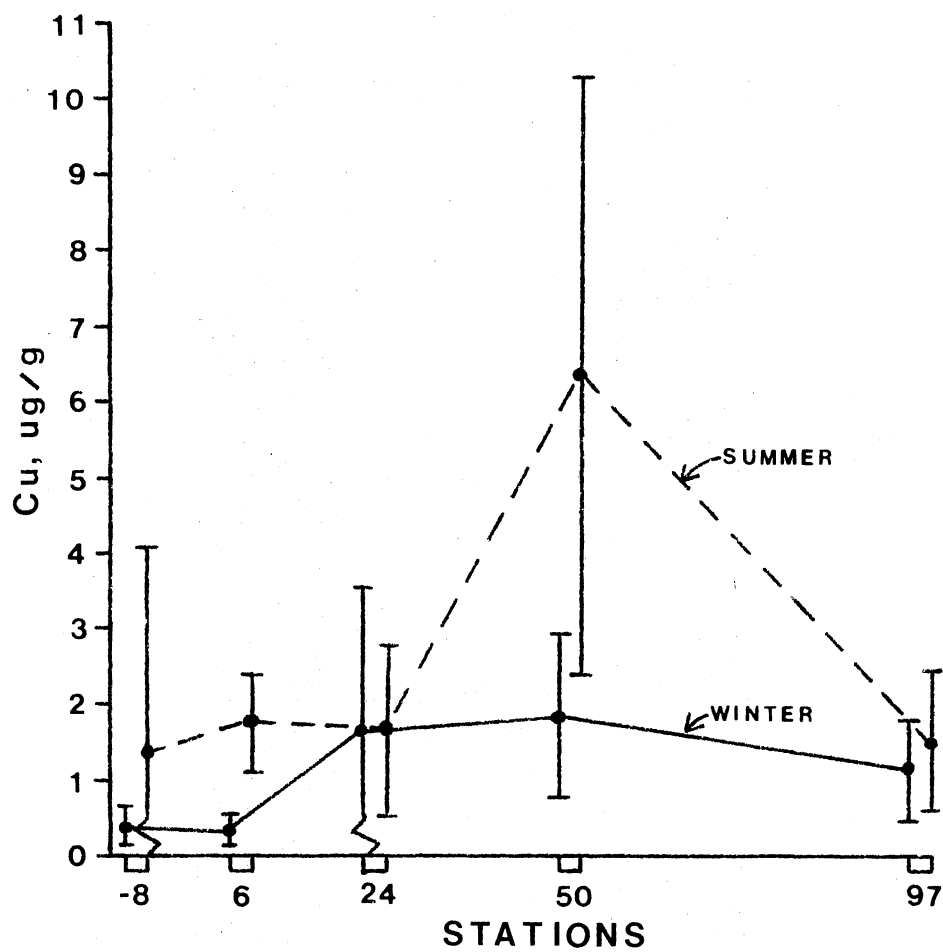


Figure 12. Mean Copper Concentration in Sediments  $\pm$  Standard Deviations for Each Station in Winter and Summer Seasons

(Table XV, Appendix). Station 50 was significantly different from the other four stations in summer. The high concentration at Station 50 may have been influenced by organic matter and particle size composition of sediments.

Loss on ignition increased to a maximum at Station 50 and closely paralleled copper concentration (Figures 12 and 13). Variation among stations of loss on ignition in Skeleton Creek sediments was significant in winter and summer seasons ( $0.010 < p < 0.025$ ). The Protected LSD test showed that Station -8 was significantly different from other stations in summer (Table XVI, Appendix). Linear regression analyses were used to see if copper concentration depended on percent loss on ignition (Figures 14 and 15). Station -8 values were not included in the regression analyses because downstream stations received heavy metals from domestic and industrial wastes which could not have influenced the upstream station. Although the winter regression coefficient was not significantly different from zero, the summer regression coefficient was different ( $p < 0.001$ ).

Particle size composition of sediments increased in the  $<0.5$  mm fraction particle size with distance downstream (Figure 16). Highly significant variation of the  $<0.5$  mm particle size existed among stations ( $p < 0.0005$ ). Protected LSD tests revealed that Stations 50 and 97 were significantly higher than Stations 6 and 24 in both seasons (Table XVII, Appendix). Stations 50 and 97 were not significantly different from each other in summer.

Organic content of lake sediments was positively correlated with fine silt and clay and negatively correlated with coarse silt and sand (Norton 1968). A similar correlation probably exists in streams.

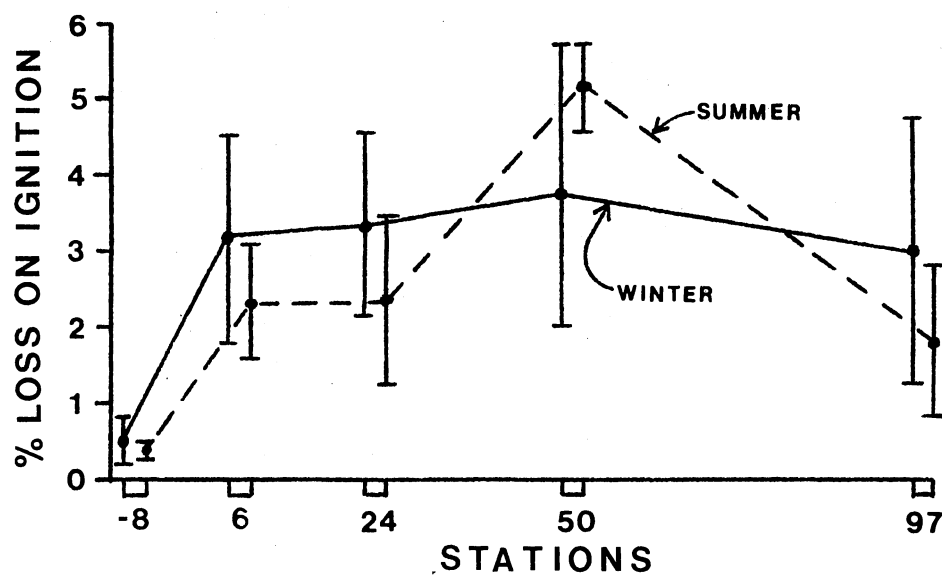


Figure 13. Mean Percent Loss on Ignition  $\pm$  Standard Deviations in Sediments for Each Station in Winter and Summer Seasons



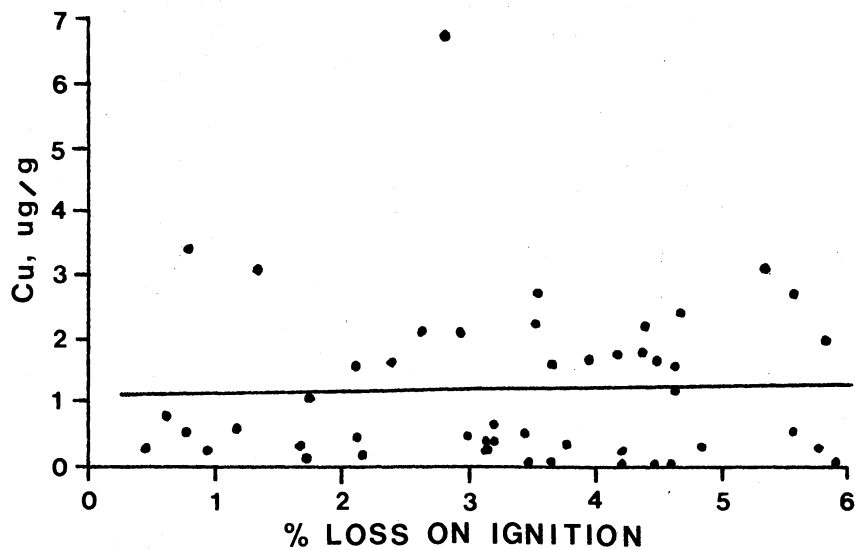


Figure 14. Regression of Copper on Percent Loss on Ignition in Sediments for Winter Data

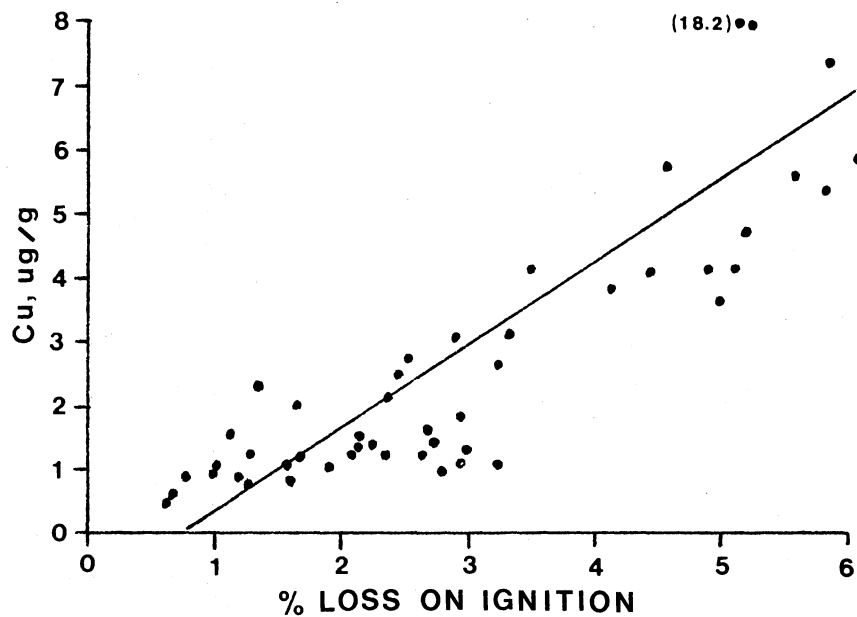


Figure 15. Regression of Copper on Percent Loss on Ignition in Sediments for Summer Data

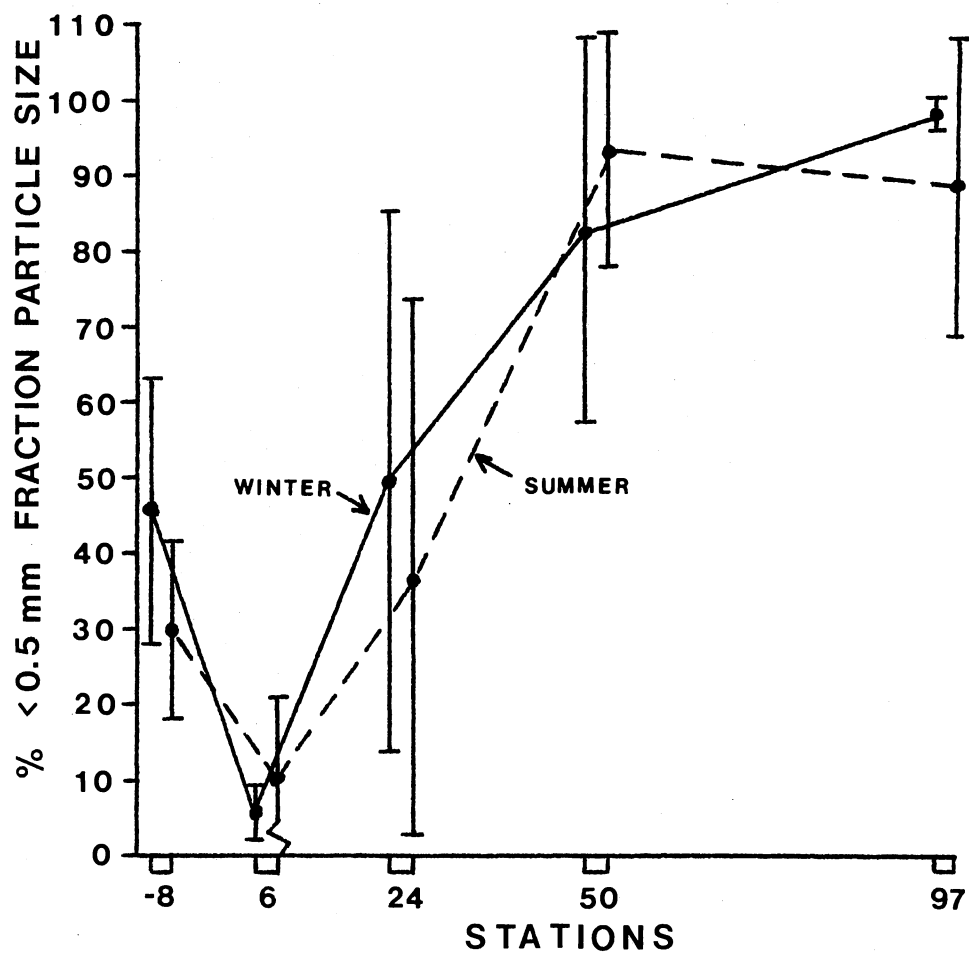


Figure 16. Mean Percent of the <0.5 mm Fraction Particle Size  $\pm$  Standard Deviations in Sediments for Each Station in Winter and Summer Seasons

Because the greatest percentage of <0.5 mm particle size was at Station 50 in summer, the increase of organic matter at Station 50 in summer possibly was influenced by particle size distribution. Environmental factors such as pH, temperature, and discharge may have increased deposition of colloidal and fine suspended material in summer, which ultimately increased the copper concentration.

Few studies have reported seasonal variation of copper in stream sediments. Potomac River Estuary sediments contained higher copper concentration in summer than in winter (Pheiffer 1972). Summer means were generally above 40  $\mu\text{g/g}$  while winter means were around 20  $\mu\text{g/g}$ . This trend corresponds to that observed in Skeleton Creek. Seasonal variation may be explained partly by the effect of temperature on microbial populations in the sediment. Higher temperature and the corresponding increase in microbial activity results in greater metal accumulation in sediments. Duke et al. (1966) reported increased zinc accumulations at a higher temperature in laboratory experiments using estuarine sediments. Similar increases may occur with other metals.

Spatial variations in copper concentration have been related to effluents, organic matter, and particle size by some investigators, but were not related to these factors by others. Copper in the Potomac River Estuary showed a slight trend of decreasing concentration with distance downstream (Pheiffer 1972). Increased concentration at several locations was thought to have come from copper in effluents entering the estuary. Organic matter content and particle size composition of sediments were not reported for the estuary. Pasternak (1974) concluded that the trace metal content in the River Biala Przemsza, Poland, depended on pollution source and not on sediment organic matter and

particle size composition. Skeleton Creek sediment data do not support these findings because the station nearest the pollution outfall did not have the highest copper concentration. The station with the highest level also had the highest loss on ignition. All station means in the Black Warrior River, Alabama, were below 1  $\mu\text{g/g}$  even though effluents entering the river contained copper approaching 1,000  $\mu\text{g/l}$  (Williams et al. 1973). Increased copper concentration with distance downstream occurred in Upper Peoria Lake (Collinson and Shimp 1972). The copper increase was directly related to organic carbon content and to a lesser degree to the  $<0.2 \mu$  clay fraction. This trend corresponds to that observed in Skeleton Creek.

An inverse relationship existed between copper level and particle sizes in the Ottawa and Rideau River sediments (Oliver 1973). Copper averaged 25  $\mu\text{g/g}$  in the 0.004 to 0.062 mm size and 9  $\mu\text{g/g}$  in the 0.5 to 2.0 mm size. This relationship was attributed to greater surface area for adsorption in the small particle sizes. Several other authors have reported that heavy metals were adsorbed on sediment particles and associated with organic matter (Gibbs 1973; Reimer and Toth 1970; Shimp et al. 1971, 1970). Surface adsorbed metals are not firmly bound to the particles but are exchangeable readily with other ions, and thus, are biologically available.

Surface adsorbed copper concentration in August samples was less than 0.10  $\mu\text{g/g}$  in Skeleton Creek sediments extracted with ammonium acetate (Figure 17). February samples were not extracted with ammonium acetate and thus no estimate of surface adsorbed copper was available. The data indicated that copper in sediments was not greatly affected by surface adsorption even though samples composed of smaller particle

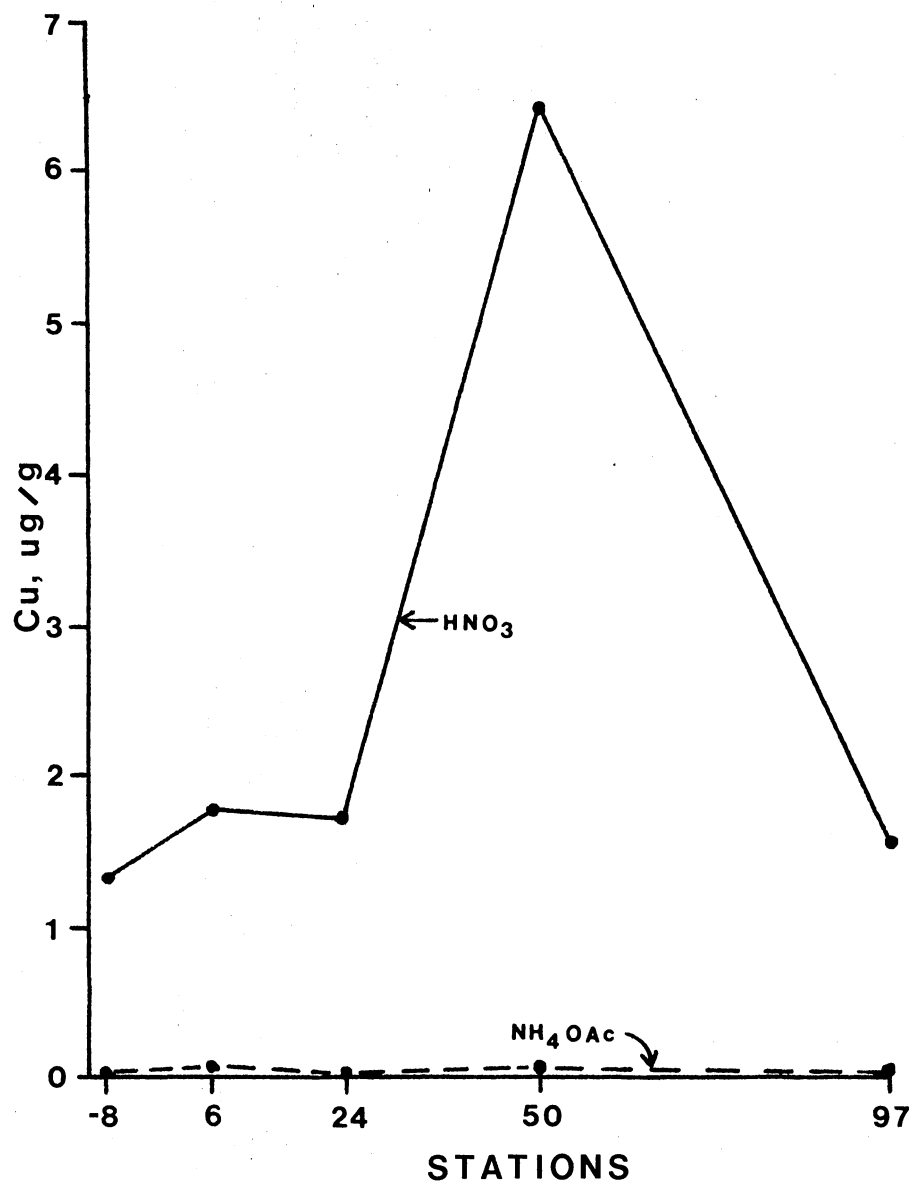


Figure 17. Mean Copper Concentration for Each Station of August Samples Extracted With 1 N Ammonium Acetate (NH<sub>4</sub>OAc) and 1 N Nitric Acid (HNO<sub>3</sub>)

sizes generally had a higher copper level. Joe Mill Creek and the Tennessee River were similar to Skeleton Creek in that ammonium acetate was ineffective in removing copper from sediments and higher concentrations were associated with smaller particle sizes of sediment (Perhac 1974). Most of the copper in the Tennessee streams was associated with carbonates and free iron oxides while minor amounts occurred with organic matter, clay structural positions, adsorption surfaces, and with sulfides. Copper associations with carbonates and iron oxides in Skeleton Creek sediments is probable because the major soil in the area, Renfrow-Zaneis-Vernon association, is rich in both carbonates and iron (Gray and Galloway 1959).

The mean chromium content in Skeleton Creek sediments of  $5.2 \mu\text{g/g}$  is much lower than values reported for other rivers. Sediments of the Illinois River had a mean chromium concentration of  $17 \mu\text{g/g}$  (Mathis and Cummings 1973) and those of the Mississippi River had a mean of  $12 \mu\text{g/g}$  (Morris et al. 1972). Ottawa and Rideau River sediments had chromium means of 22 and  $21 \mu\text{g/g}$ , respectively (Oliver 1973). Mean concentration in the Potomac River Estuary ranged from less than 20 to over  $70 \mu\text{g/g}$  (Pheiffer 1972). Skeleton Creek chromium concentration possibly was low because of high stream discharge and scouring of the stream bed prior to sampling.

Chromium concentration in the sediments collected in warm water conditions was significantly greater than that in cool water ( $0.010 < p < 0.025$ ) (Figure 18). Station 50 had the maximum chromium level in both seasons and Station -8 had the minimum level. Variation among station means in Skeleton Creek was highly significant ( $p < 0.0005$ ). Chromium means ranged from 1.3 to  $6.3 \mu\text{g/g}$  in winter and

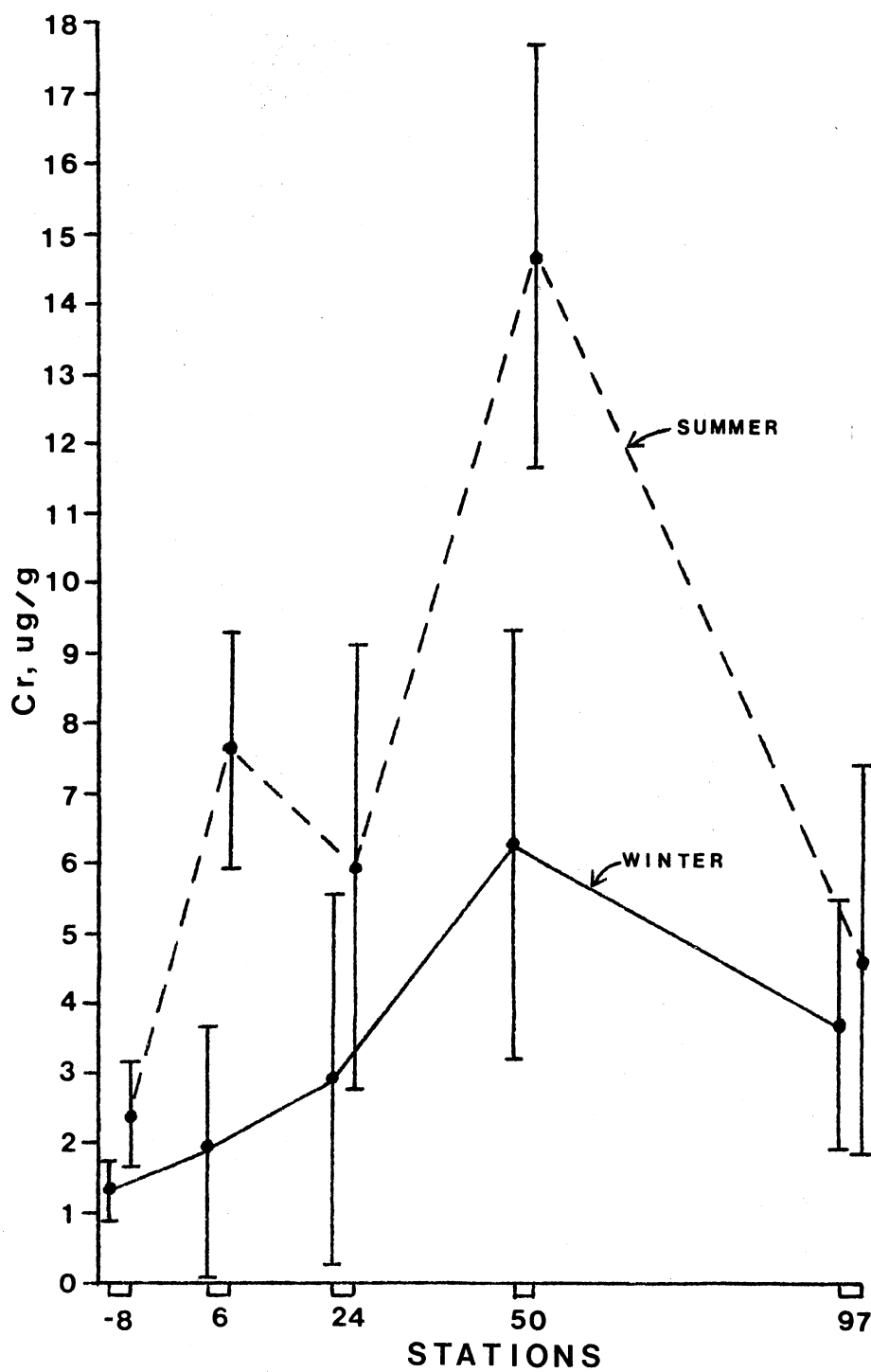


Figure 18. Mean Chromium Concentration in Sediments  $\pm$  Standard Deviations for Each Station in Winter and Summer Seasons

from 2.4 to 14.7  $\mu\text{g/g}$  in summer. The Protected LSD test indicated that Station 50 was significantly different from other stations in both seasons (Table XVIII, Appendix). Station -8 was different from other stations in summer. High chromium level at Station 50 was influenced by organic content and particle size of sediments.

Loss on ignition and chromium concentrations increased from a minimum at Station -8 to a maximum at Station 50 (Figures 13 and 18). Protected LSD tests showed significant differences for Stations -8 and 50 (Table XVI, Appendix). Linear regression analyses revealed that chromium concentration was associated with percent loss on ignition in winter but was not in summer (Figures 19 and 20). The difference between the summer regression coefficient and zero was highly significant ( $p < 0.001$ ).

Greater amounts of the  $<0.5$  mm particle size at downstream stations (Figure 16) and the positive correlation of organic matter with fine particles may have affected spatial variation of chromium. Higher chromium level in summer at Station 50 may have occurred because loss on ignition and the  $<0.5$  mm particle size fraction were both higher in summer than in winter.

Chromium concentration in the sediments of the Potomac River Estuary had a small difference between summer and winter (Pheiffer 1972). The higher level in summer in Skeleton Creek may be a reflection of greater microbial activity at higher water temperature.

Effluents, organic matter, and particle size have been reported by several investigators to have affected spatial variation of chromium in sediments of streams and rivers. Chromium concentration in sediments tended to decrease slightly with distance downstream in the Potomac



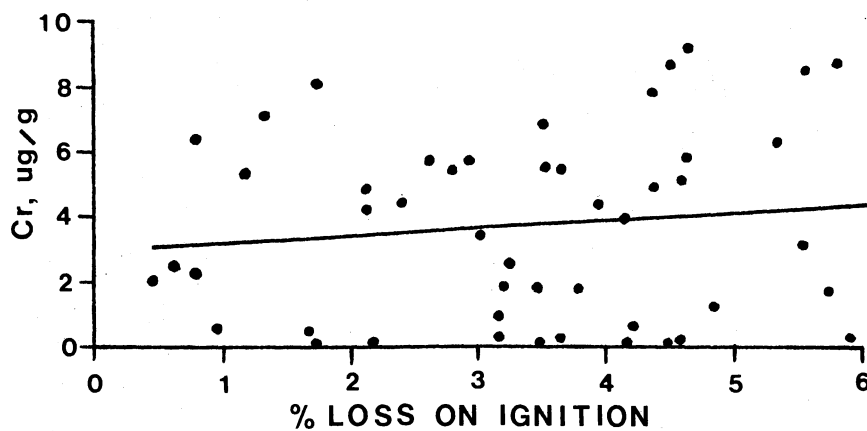


Figure 19. Regression of Chromium on Percent Loss on Ignition in Sediments for Winter Data

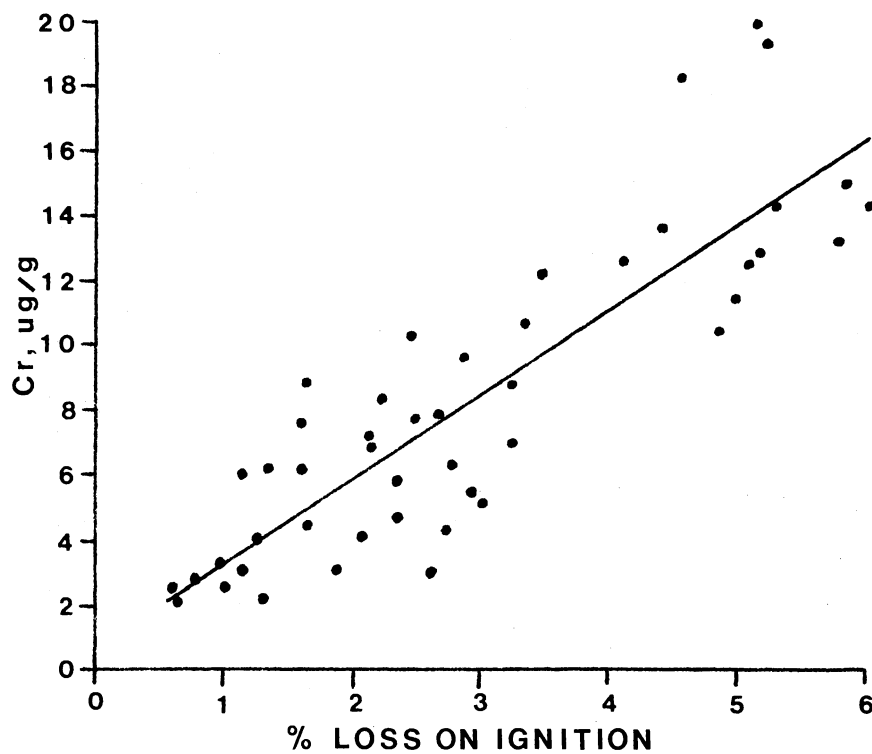


Figure 20. Regression of Chromium on Percent Loss on Ignition in Sediments for Summer Data

River Estuary (Pheiffer 1972). An increase occurred below pollution outfalls. No associations with organic matter or particle size composition were attempted. Spatial variation of metals in the River Biala Przemsza, Poland, was influenced by degree of pollution (Pasternak 1974). No connection existed between organic content or particle size composition and metal levels in sediments. Skeleton Creek data are in contrast to these studies. Although the Black Warrior River, Alabama, received wastes containing a low level of chromium, no spatial variation was evident (Williams et al. 1973). Collinson and Shimp (1972) found a large variation among stations, but no general trend. Chromium distribution did not show a dependency on organic content and  $<2 \mu$  clay fraction in Upper Peoria Lake although it existed in Lake Michigan (Shimp et al. 1971, 1970).

A positive correlation existed between chromium levels and small particles in Ottawa and Rideau River sediments (Oliver 1973). Chromium averaged 27 and 9  $\mu\text{g/g}$  for particle size ranges 0.004 to 0.062 mm and 0.5 to 2.0 mm, respectively. Greater surface area for metal adsorption on smaller particle sizes was responsible for these differences.

August samples of Skeleton Creek sediments extracted with ammonium acetate showed that chromium did not exist as surface adsorbed cations (Figure 21). All means were less than 0.05  $\mu\text{g/g}$  in the ion exchangeable fraction, while the nitric acid extraction means were all greater than 2  $\mu\text{g/g}$ . These data support the findings of Perhac (1974) in which ammonium acetate removed only minor amounts of chromium from Joe Mill Creek and Tennessee River sediments. As in Skeleton Creek, surface adsorption was suspected in the Tennessee streams because smaller particle sizes were found in areas of high chromium concentrations. Chromium

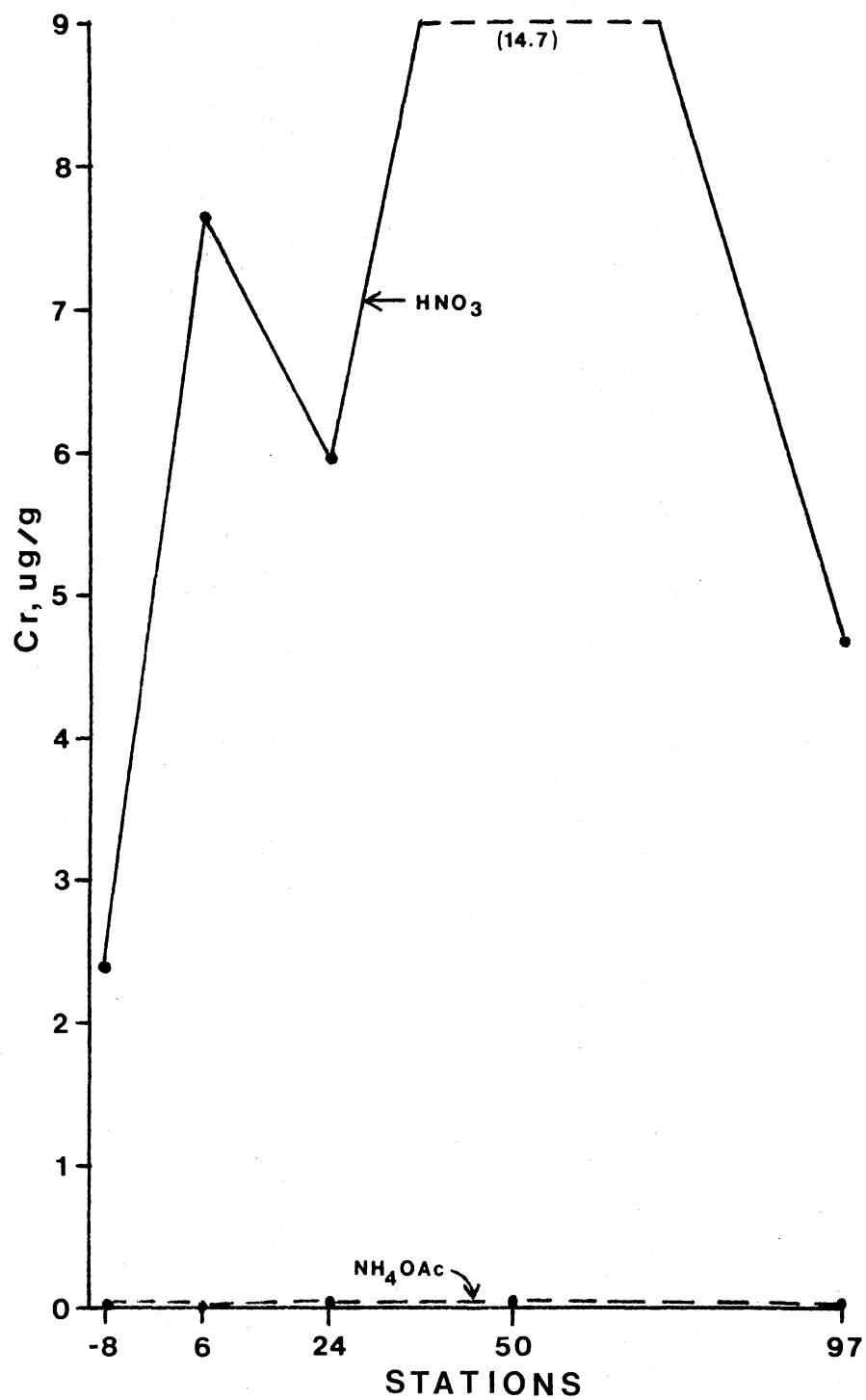


Figure 21. Mean Chromium Concentration for Each Station of August Samples Extracted With 1 N Ammonium Acetate ( $\text{NH}_4\text{OAc}$ ) and 1 N Nitric Acid ( $\text{HNO}_3$ )

distribution in the Tennessee streams was governed by carbonate and iron oxide associations and these associations probably occur in Skeleton Creek.

Lead concentration in Skeleton Creek sediments averaged  $3.5 \mu\text{g/g}$ , which is over 10 times smaller than the  $42 \mu\text{g/g}$  mean for the Rideau River, Canada (Oliver 1973). The Ottawa River mean of  $26 \mu\text{g/g}$  was also considerably higher than values in Skeleton Creek. Illinois and Mississippi River sediments had means of 28 and  $14 \mu\text{g/g}$ , respectively (Mathis and Cummings 1973; Morris et al. 1972). Potomac River Estuary sediments ranged from 20 to  $60 \mu\text{g/g}$  (Pheiffer 1972). Lead in sediments of Lake Carl Blackwell averaged  $25 \mu\text{g/g}$  (Sias 1974) and the mean in Theta Pond was  $529 \mu\text{g/g}$  (Namminga et al. 1974). High stream discharge and scouring of the stream bed prior to sampling may be responsible for the low lead levels in Skeleton Creek.

Although Skeleton Creek generally contained a higher lead concentration in sediments in summer than in winter (Figure 22), the difference between seasons was not significant ( $0.1 < p < 0.25$ ). Cool season means ranged from  $1.0 \mu\text{g/g}$  at Station 6 to  $6.2 \mu\text{g/g}$  at Station 50. The highest warm season mean of  $10.1 \mu\text{g/g}$  occurred also at Station 50, but the smallest mean of  $1.0 \mu\text{g/g}$  existed at Station -8. Differences in means among stations in Skeleton Creek were highly significant ( $p < 0.0005$ ). The Protected LSD test showed that Station 50 was significantly different from the other four stations in both seasons (Table XIX, Appendix). In addition, Station 6 was different from Stations 24 and 97 in winter and Station -8 was different from Stations 6 and 24 in summer. High organic content and small particle size composition of sediments were probably more important factors influencing the high

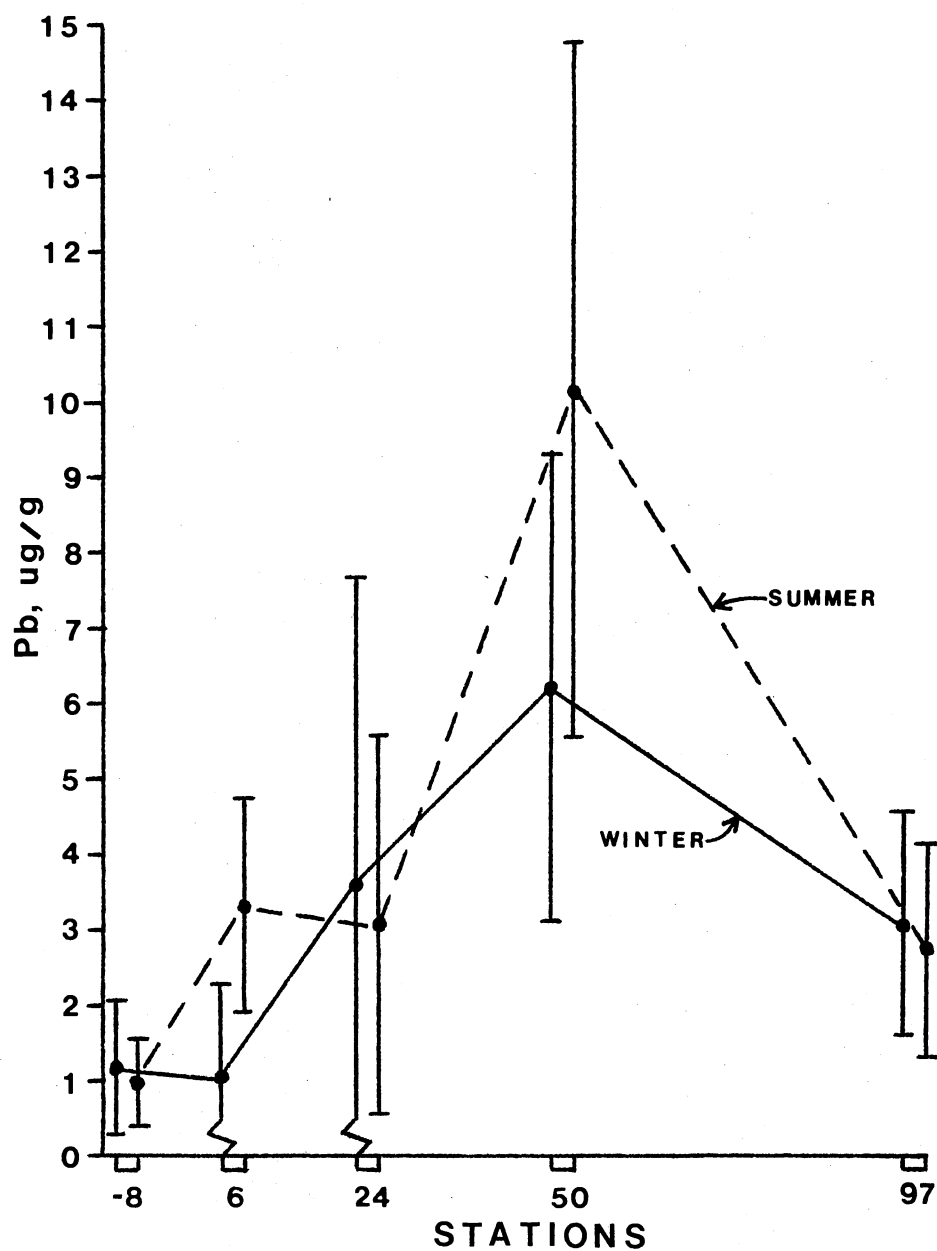


Figure 22. Mean Lead Concentration in Sediments  
± Standard Deviations for Each  
Station in Winter and Summer  
Seasons

lead level at Station 50.

Minimum values of percent loss on ignition and lead concentration at Station -8 increased to maximum levels at Station 50 (Figures 13 and 22). Although the lead concentration was not related to loss on ignition in winter, the relationship existed in summer when tested by linear regression analyses (Figures 23 and 24). The summer regression coefficient was significantly different from zero ( $p < 0.001$ ).

Sediments with a smaller mean particle size that occurred at downstream stations (Figure 16) may have influenced organic matter distribution, and ultimately, the lead distribution in Skeleton Creek. Fine sediment particles were positively correlated with organic matter in Lake Carl Blackwell (Norton 1968). Higher summer concentration of lead at Station 50 may be the result of high  $<0.5$  mm particle size fraction and organic content at this station.

Little seasonal variation of lead existed in the sediments of the Potomac River Estuary (Pheiffer 1972). Differences in summer and winter means were small also in Skeleton Creek although slightly higher levels existed at some stations in summer. The higher summer levels may have resulted from higher microbial activity at higher water temperature.

Spatial variation of lead in sediments has been related to effluents, organic matter, and particle size in some aquatic systems, but the relationship was absent in others. Lead in the Potomac River Estuary generally declined with distance downstream although a higher level was recorded near pollution outfalls (Pheiffer 1972). No trend was evident in winter, but a higher concentration occurred below the sources of effluents. Pasternak (1974) reported that metal concentrations increased near pollution and were not associated with organic matter or

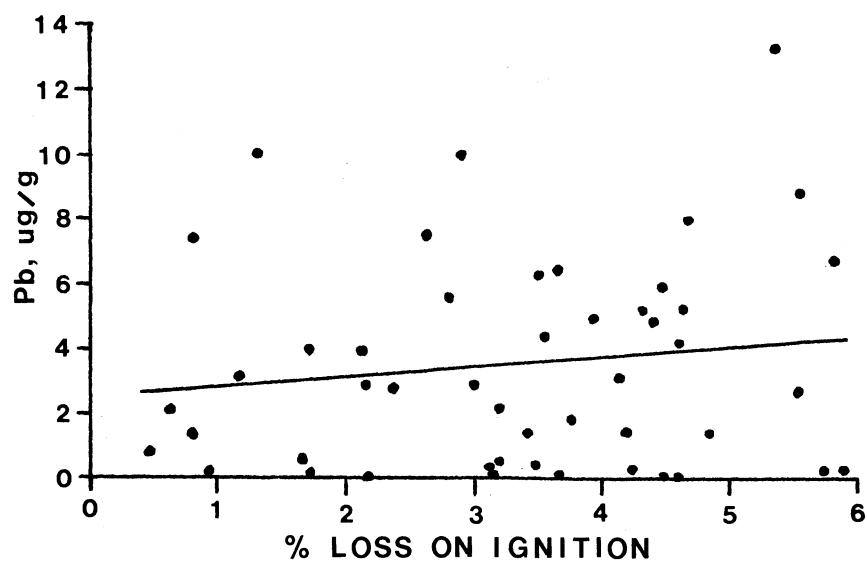


Figure 23. Regression of Lead on Percent Loss on Ignition in Sediments for Winter Data

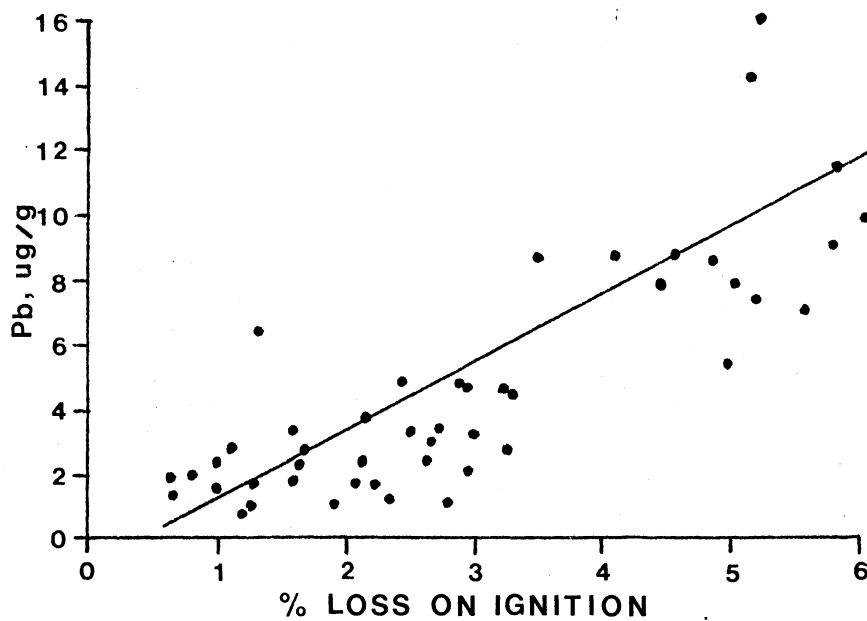


Figure 24. Regression of Lead on Percent Loss on Ignition in Sediments for Summer Data

silt content of the sediments. The lead distribution in Skeleton Creek does not support this finding because a higher level was found associated with organic matter and smaller particle sizes at stations farther downstream than those near the outfall. Upper Peoria Lake sediments contained a higher concentration at downstream stations, and the increase was directly related to organic carbon content and the <2  $\mu$  clay fraction (Collinson and Shimp 1972). Similar trends have been reported in several other aquatic systems (Gibbs 1973; Riemer and Toth 1970; Shimp et al. 1971, 1970).

An inverse relationship existed between lead level and particle size in the Ottawa and Rideau Rivers, Canada (Oliver 1973). Particle sizes ranging from 0.004 to 0.062 mm contained 33  $\mu\text{g/g}$  while only 5  $\mu\text{g/g}$  occurred in the 0.5 to 0.2 mm range. Greater surface area for adsorption of metals on the smaller particles was responsible for the relationship. No estimation was made of organic matter content of sediments.

Ammonium acetate extractions of Skeleton Creek sediments which were collected in August showed that lead was not located in exchangeable sites on particle surfaces. No samples contained lead above detection limit concentration. Similarly, ammonium acetate extractions of Tennessee River sediments showed that lead was not surface adsorbed even though sediments of finer particle sizes contained higher concentrations (Perhac 1974). Lead in the Tennessee River was primarily associated with carbonates and free iron oxides and to a lesser extent with organic matter, clay structure, adsorption surfaces, and sulfides. Skeleton Creek sediments contain high levels of carbonates and iron.

Skeleton Creek had a mean zinc concentration of 9.2  $\mu\text{g/g}$ , which is considerably smaller than most values reported in the literature. Zinc



means ranged from 8.7  $\mu\text{g/g}$  in the Newport River Estuary (Cross et al. 1970) to 400  $\mu\text{g/g}$  in the Potomac River, Maryland (O'Connor et al. 1964). Mean zinc levels were 84 and 86  $\mu\text{g/g}$  in the Ottawa and Rideau Rivers, Canada (Oliver 1973), 81  $\mu\text{g/g}$  in the Illinois River (Mathis and Cummings 1973), and 79  $\mu\text{g/g}$  in the Mississippi River (Morris et al. 1972). Low zinc concentration in Skeleton Creek possibly resulted from high stream discharge and scouring of the stream bed prior to sampling.

Zinc concentration was higher in the summer than in the winter (Figure 25). Seasonal variation was statistically significant ( $0.001 < p < 0.005$ ). Minimum and maximum zinc concentrations occurred at Stations -8 and 50, respectively, in both seasons. Differences in sediment zinc concentration among the five stations were highly significant ( $p < 0.0005$ ). Zinc means in winter ranged from 2.2  $\mu\text{g/g}$  at Station -8 to 9.2  $\mu\text{g/g}$  at Station 50, while summer means ranged from 2.3 to 26.6  $\mu\text{g/g}$  at the same stations. The Station 50 summer mean was nearly three times the winter mean. Protected LSD tests found that Stations -8 and 97 were different from the other three stations, but were not different from each other (Table XX, Appendix). In summer, all stations were significantly different from all other stations. Factors that influenced the high zinc level at Station 50 probably include organic content and particle size composition of the sediments.

Minimum values of percent loss on ignition and zinc concentrations occurred at Station -8 and increased to maximum levels at Station 50 (Figures 13 and 25). Linear regression analyses were conducted to test if the zinc level depended on loss of ignition (Figures 26 and 27). The regression coefficient in winter was not significantly different

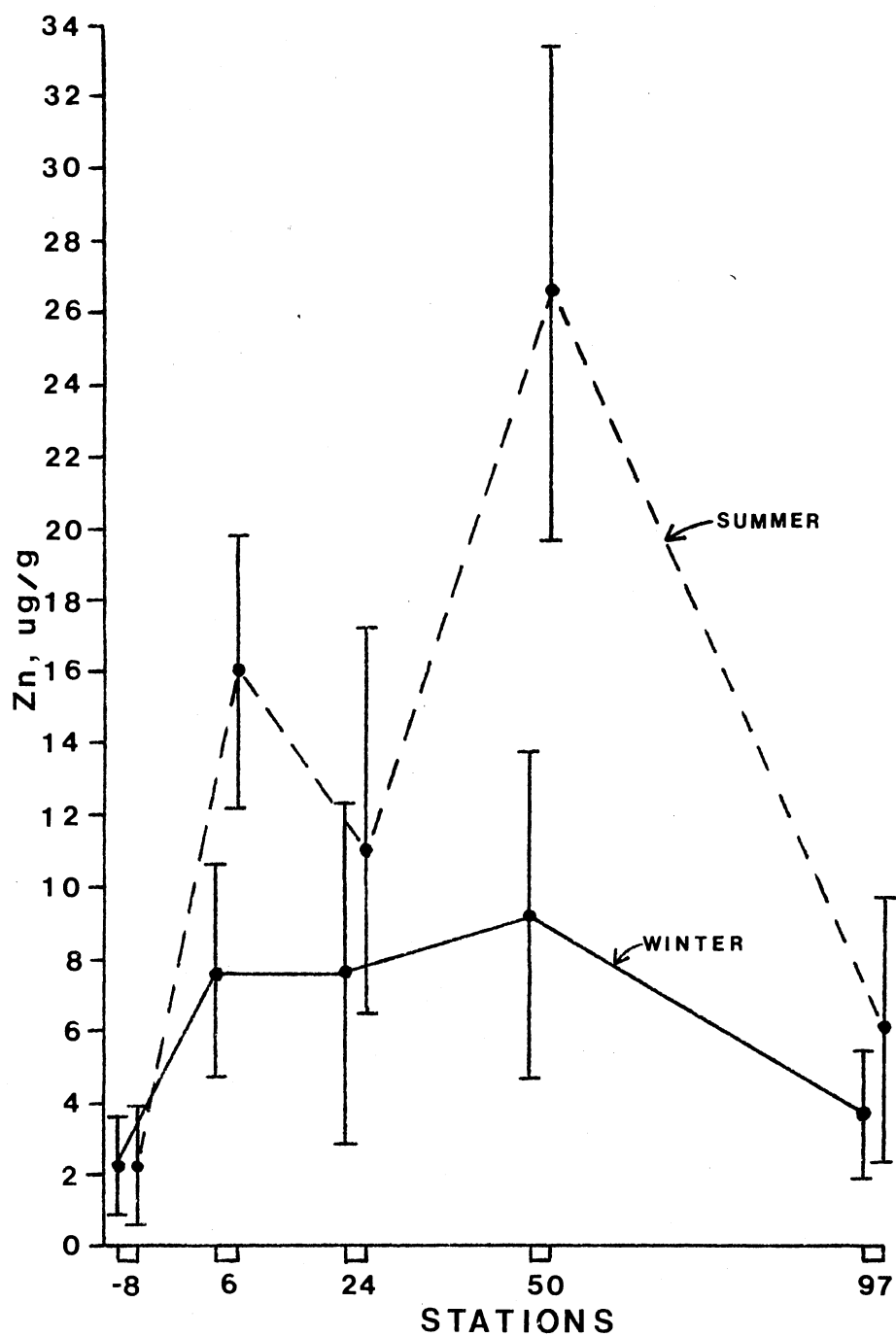


Figure 25. Mean Zinc Concentration in Sediments  $\pm$  Standard Deviations for Each Station in Winter and Summer Seasons

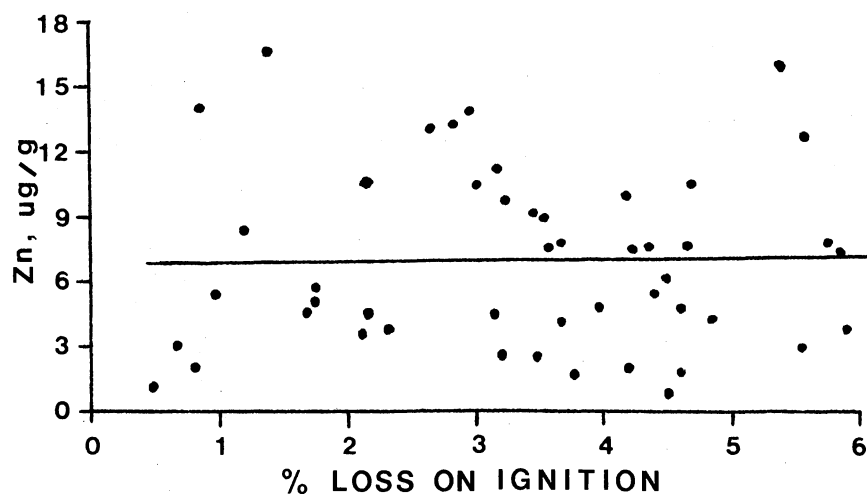


Figure 26. Regression of Zinc on Percent Loss on Ignition in Sediments for Winter Data

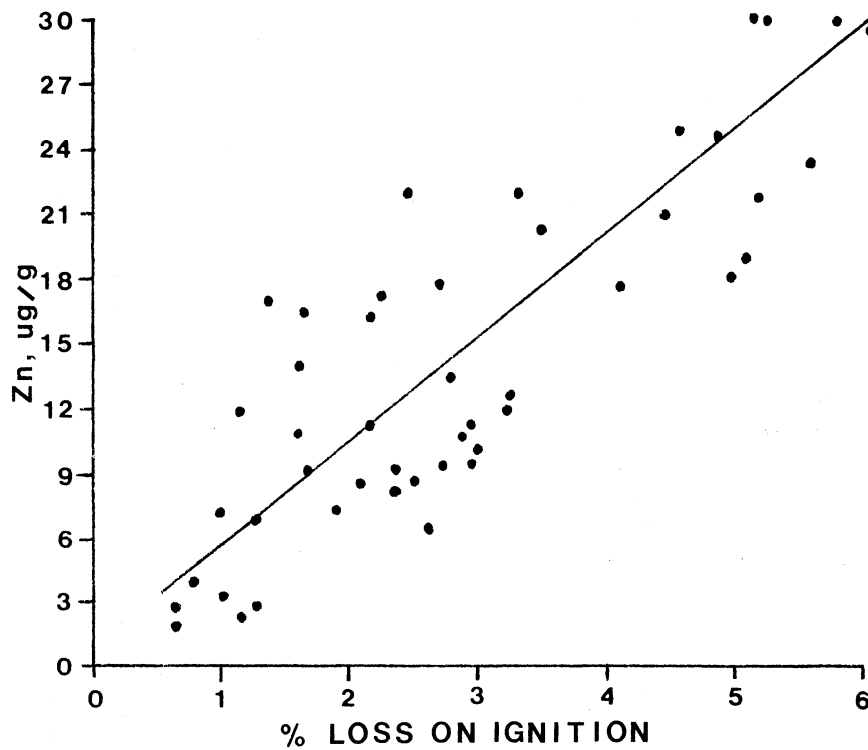


Figure 27. Regression of Zinc on Percent Loss on Ignition in Sediments for Summer Data

from zero while the summer coefficient difference was highly significant ( $p < 0.001$ ).

The  $<0.5$  mm particle size fraction increased at downstream stations (Figure 16) and may have indirectly influenced the zinc distribution in Skeleton Creek sediments. Norton (1968) found that finer sediment particles were positively correlated with organic matter in Lake Carl Blackwell. A similar condition may exist in Skeleton Creek. Because Station 50 had a higher percentage of the finer sediments, possibly a greater accumulation of organic material occurred, and thus, a higher zinc mean.

Seasonal variation of zinc in the Potomac River Estuary, if present, was not detected due to the large range of means for stations in winter samples (Pheiffer 1972). The wide range of zinc concentration was attributed to increased freshwater flow into the estuary during December. Similarly, no seasonal pattern of zinc distribution existed in the Newport River Estuary (Cross et al. 1970). Although Duke et al. (1966) experimented with estuarine sediments under laboratory conditions, it was found that zinc accumulated to a higher level at higher temperature. It was believed that increased temperature allowed greater microbial activity, and ultimately, greater zinc accumulation. A higher summer level of zinc in Skeleton Creek probably reflects microbial activity.

Contrasting relationships between the spatial variation in zinc concentration and effluents, organic matter, and particle size have been reported. Potomac River Estuary sediments contained a higher concentration at stations below pollution outfalls (Pheiffer 1972). Extremely wide fluctuations of station means occurred in winter samples. For example, two stations within 30 km of each other varied in

concentration from less than 200  $\mu\text{g/g}$  to over 1,000  $\mu\text{g/g}$ . Zinc concentration in the River Biala Przemsza, Poland, depended on a source of pollution and not on organic matter or silt particles in the sediments (Pasternak 1974). The highest zinc concentrations (5,000 to 10,000  $\mu\text{g/g}$ ) in the Black Warrior River, Alabama, occurred at the upstream station near sources of pollution (Williams et al. 1973). The following station located about 50 km downstream had much lower levels (0.3 to 1.0  $\mu\text{g/g}$ ), while the remaining two stations had higher concentrations (2,000 to 5,000  $\mu\text{g/g}$ ). No explanation was given for the spatial variation. The trend found in Skeleton Creek does not correspond to these studies.

Organic matter and particle size composition were important in other studies. Newport River Estuary had a reduced zinc level at stations located in the seaward direction (Cross et al. 1970). The seaward stations had higher percentages of sand in the sediments. Muddy sediments contained a higher concentration than did sandy ones. Zinc concentration increases in Upper Peoria Lake sediments were directly related to organic carbon content and, to a lesser extent, to the  $<2 \mu$  clay fraction (Collinson and Shimp 1972). This relationship corresponds to that in Skeleton Creek and it has been found in several other studies (Gibbs 1973; Riemer and Toth 1970; Shimp et al. 1971, 1970). Ottawa and Rideau River sediments exhibited an inverse relationship between zinc concentrations and particle size (Oliver 1973). The mean of 0.004 to 0.062 mm particle sizes was 88  $\mu\text{g/g}$ , while the 0.5 to 2.0 mm mean was 24  $\mu\text{g/g}$ . Smaller particles having greater surface areas for zinc adsorption were the responsible factor.

Skeleton Creek sediments extracted with ammonium acetate demonstrated that surface adsorbed zinc was not important (Figure 28). Zinc

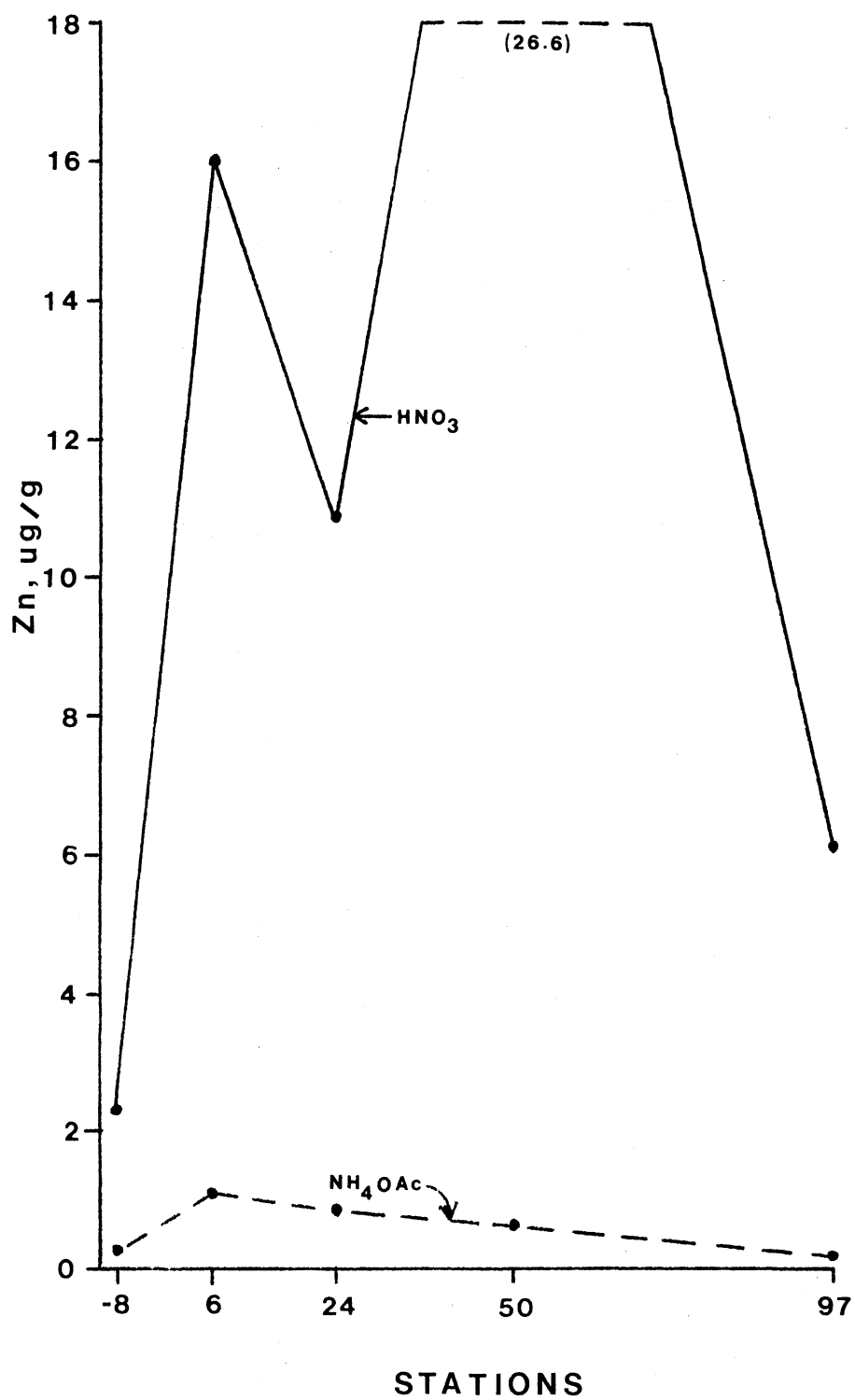


Figure 28. Mean Zinc Concentration for Each Station of August Samples Extracted With 1 N Ammonium Acetate (NH<sub>4</sub>OAc) and 1 N Nitric Acid (HNO<sub>3</sub>).

concentrations in the ion exchangeable fraction were near and below 1  $\mu\text{g/g}$ , while nitric acid extraction means were much greater than 2  $\mu\text{g/g}$ , with one exception. The findings in Skeleton Creek support those of Perhac (1974) in which ammonium acetate removed only minor amounts of zinc from Joe Mill Creek and Tennessee River sediments. Carbonates and iron oxides were the major factors responsible for influencing zinc distribution in the Tennessee streams. A smaller zinc level was probably associated with organic matter, clay structures, adsorbed on surfaces, and with sulfides. A similar condition may have existed in Skeleton Creek.

#### Copper, Chromium, Lead, and Zinc in Chironomids

Copper concentrations of chironomid larvae from Skeleton Creek collected at Station 6 in August averaged 1.91  $\mu\text{g/g}$  (Table VII). This mean is slightly higher than the mean of 1.77  $\mu\text{g/g}$  for sediments, but is much higher than the 3.5  $\mu\text{g/l}$  mean for water. The concentration factors of 1.1 for sediments and 550 for water were smaller than those for Illinois River tubificids (Mathis and Cummings 1971). Tubificids concentrated copper 1.3 times the mean in sediments and 21,800 times over the level in water. Theta Pond benthos, consisting mostly of tubificids and chironomids, had a mean of 230  $\mu\text{g/g}$ , which is considerably larger than the Skeleton Creek mean (Namminga et al. 1974). Benthos concentrated copper over the level in water by a factor of 46,800, while a smaller ratio of 4.6 existed for benthos and sediments.

Chromium in Skeleton Creek chironomids averaged 2.96  $\mu\text{g/g}$ , which is lower than the 7.64  $\mu\text{g/g}$  mean for sediments at the same station (Table

VII). The concentration factor was only 0.39 for sediments but midge larvae had a concentration 2,960 times the mean for water. Similarly, chromium was less concentrated in tubificids than in sediments of the Illinois River (Mathis and Cummings 1971). The tubificids accumulated chromium above the water level by a factor of 420.

TABLE VII  
CONCENTRATIONS OF HEAVY METALS IN CHIRONOMIDS

Dates	Metal ( $\mu\text{g/g}$ )			
	Cu	Cr	Pb	Zn
23 Aug 73				
rep 1	1.87	3.98	1.17	74.98
rep 2	1.42	3.24	1.01	54.70
25 Aug 73				
rep 1	2.00	2.29	1.43	51.49
rep 2	2.35	2.35	1.68	47.11
Mean	1.91	2.96	1.32	57.07
(S.D.)	(0.38)	(0.80)	(0.30)	(12.34)

Although lead concentration in Skeleton Creek chironomids was the lowest of the four metals (Table VII), lead possibly had the highest accumulation ratio. Lead was below the level of detection in August water samples, while  $1.32 \mu\text{g/g}$  was measured in the midge larvae. The low concentration factor of 0.40 reflected the lowest level in midges compared to that in sediments. Both water and tubificid concentrations of lead were considerably higher in the Illinois River (Mathis and



Cummings 1971). The concentration factor of tubificids over water was 7,500, the highest ratio determined in the Illinois River. Lead in tubificids averaged 16  $\mu\text{g/g}$ . Levels were higher in sediments than in chironomids and a ratio of only 0.57 resulted. Similarly, Theta Pond benthos had a much lower concentration than the level in sediments (Namminga et al. 1974). The benthos mean was 37  $\mu\text{g/g}$  while surface sediments averaged 529  $\mu\text{g/g}$ . In contrast to the high ratio of tubificids over water in the Illinois River, Theta Pond benthos concentrated lead 2,800 times the mean of water.

The mean zinc concentration of chironomids in Skeleton Creek was 57.07  $\mu\text{g/g}$ , which was the highest of the four metals measured (Table VII). Because the level was also high in sediments, midges accumulated zinc above the sediment level only by a factor of 3.6. A much larger concentration factor of 30,000 existed for the ratio of means of chironomids to water. Skeleton Creek data did not correspond to the findings of Mathis and Cummings (1971) in which tubificids had a much lower zinc level than sediments. The tubificid-water ratio of 1,300 was also much lower than the Skeleton Creek ratio. The concentration factor in the benthos of Theta Pond was 1.9 which is comparable to that in Skeleton Creek. The benthos contained 410  $\mu\text{g/g}$  zinc and sediments averaged 219  $\mu\text{g/g}$  (Namminga et al. 1974).

Zinc uptake in the dragonfly Plathemis lydia occurred primarily by surface adsorption and cation exchange (Kormondy 1965). Most of the metal burden was associated with the exoskeleton and was lost during ecdysis. Similar results were reported for zinc and other metals in marine copepods (Martin 1970). Metal uptake and loss in Skeleton Creek chironomids probably was governed by similar mechanisms. The low

concentrations of heavy metals in the midges compared to the sediments probably occurred because the midge larvae in warm August water would be growing and molting frequently, and thus, would be eliminating the adsorbed metals periodically.

## CHAPTER VII

### CONDITIONS FOLLOWING HIGH DISCHARGE

#### Environmental Conditions

Samples were taken from April 4 through July 4, 1973, following periods of rainfall and increased discharge. Water temperature generally increased with time (Table VIII). Mean temperature ranged from 11.5 C on April 7 to 29.5 C on July 4. Considerable variation existed in dissolved oxygen among the 12 sampling dates (Table VIII). Values ranged from 6.68 mg/l on June 4 to 10.30 mg/l on May 16.

TABLE VIII

MEAN WATER TEMPERATURE, DISSOLVED OXYGEN, AND pH

Dates	Temperature (C)	Dissolved Oxygen (mg/l)	pH
4 April 73	15.8	8.98	8.2
7 April 73	11.5	9.22	8.2
11 April 73	12.0	9.72	8.2
13 April 73	18.0	8.98	8.3
24 April 73	18.5	7.68	8.2
16 May 73	19.5	10.30	8.4
4 June 73	23.5	6.68	8.2
12 June 73	24.5	7.38	8.4
20 June 73	27.5	9.02	8.4
22 June 73	25.8	8.25	8.4
26 June 73	26.5	9.00	8.4
4 July 73	29.5	8.95	8.5

Alkalinity and turbidity were inversely related (Figure 29). Maximum alkalinity and minimum turbidity occurred on May 16 while minimum alkalinity and maximum turbidity occurred on April 11. To examine the trends over time after a rainfall, metal concentrations for specific days after rainfall of the various study periods were combined. Alkalinity increased with time after high discharge, while turbidity decreased through Day 8 followed by a slight increase on Day 16 (Figure 30). Low alkalinities during high discharge were due to dilution of alkaline effluents by rainwater and surface water runoff. Similarly, turbidity was greater during high discharge because of resuspension of surface sediments and erosion of adjacent land during runoff.

Linear regression analyses were used to test if the increase of alkalinity and the decrease of turbidity changed logarithmically with days after high discharge. Regression coefficients represented the instantaneous rate of change and depended on the levels present in the water. Changes in the rate in which alkalinity increased with time are described by the regression equation:

$$\log Y = 2.3661 + 0.0083 X$$

The regression coefficient for alkalinity was an increase of only 0.0083 log mg/l per day but was significant at the 0.06 level. The coefficient for turbidity was not significant.

Frequent rains during April, May, and June (Figure 31) caused large fluctuations in daily stream discharge (Figure 32). Daily stream discharge increased considerably after precipitation in April and May, but much less in June because of less runoff due to reduction in soil moisture.

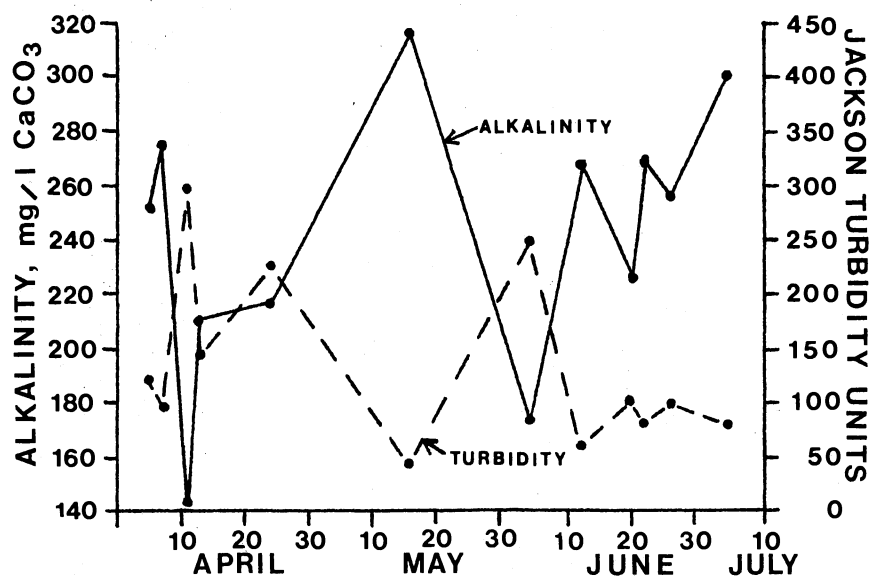


Figure 29. Mean Alkalinity and Turbidity by Sampling Dates Following High Stream Discharge

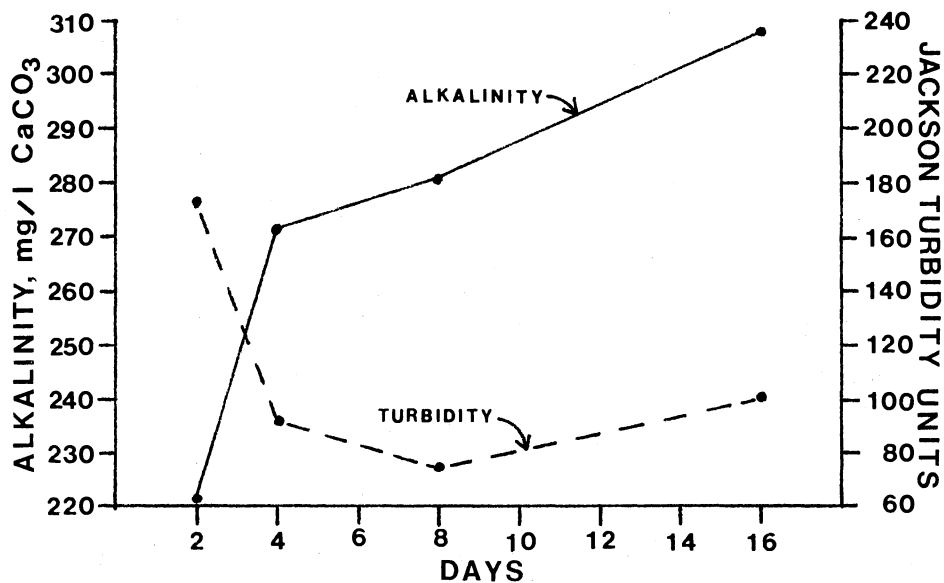


Figure 30. Alkalinity and Turbidity Means for Days After High Stream Discharge Adjusted by Multiple Regression Analysis for Differences Between Stations and Among Sampling Periods

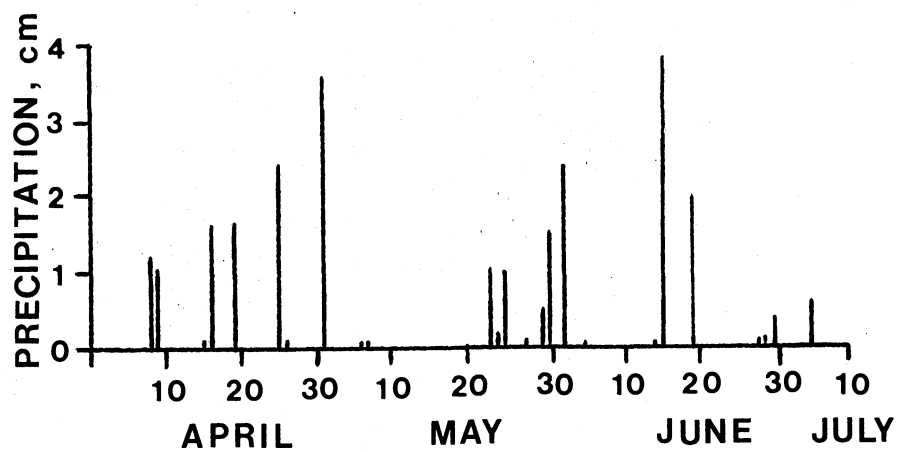


Figure 31. Daily Precipitation Recorded at Enid, Oklahoma

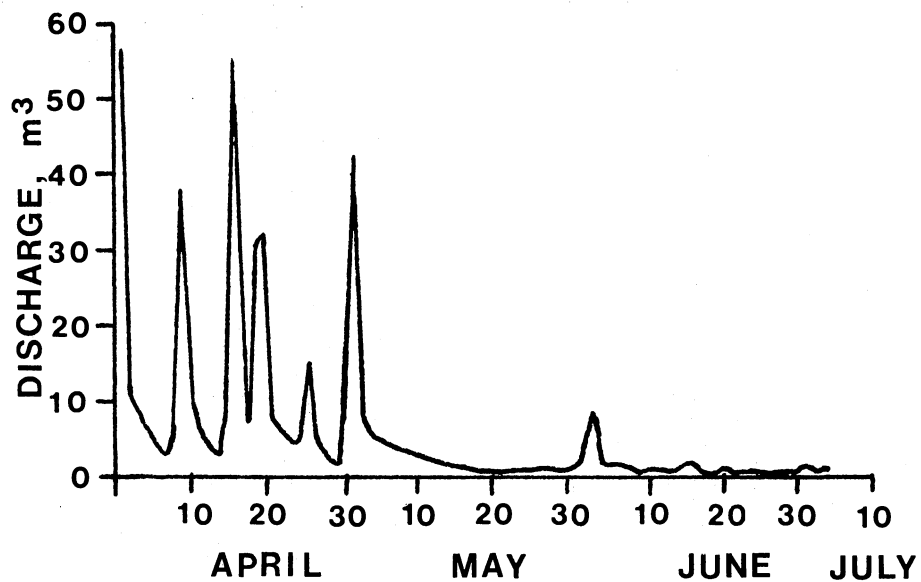


Figure 32. Mean Daily Discharge Recorded at Kilometer 76

### Copper, Chromium, and Zinc in Water

Copper concentration in Skeleton Creek generally decreased during the study (Figure 33). Means decreased from 4.9  $\mu\text{g/l}$  for samples collected after the second rain to 1.2  $\mu\text{g/l}$  for the group collected after the sixth rain. Differences among means for the groups of sampling dates after rainfall were highly significant ( $p = 0.0001$ ). These data support the observation made earlier that copper concentration in Skeleton Creek was higher in winter than in summer and probably reflects a smaller discharge of metals in effluents entering the stream in summer. A general decline in copper concentration was not observed in spring and summer months in streams of the Cayuga Lake Basin, New York (Kubota et al. 1974). Unlike Skeleton Creek, these streams were in a rural area not influenced by industrial wastes.

Combined copper concentrations of specific days after a rainfall for the various study periods decreased significantly with time ( $p = 0.02$ ) from 3.8 to 1.9  $\mu\text{g/l}$  (Figure 34). The following linear regression analysis showed that the changing rate of copper reduction approached a logarithmic curve:

$$\log Y = 0.6407 - 0.0222 X$$

The regression coefficient was significantly different from zero ( $0.001 < p < 0.01$ ), indicating that copper was reduced rapidly the first few days following high flow.

Chromium concentration generally decreased with time (Figure 35). The maximum mean of 3.4  $\mu\text{g/l}$  occurred after the April 9 rain while the minimum of 1.1  $\mu\text{g/l}$  was found following the June 19 rain. Significant differences among means for the groups of sampling dates after rainfall

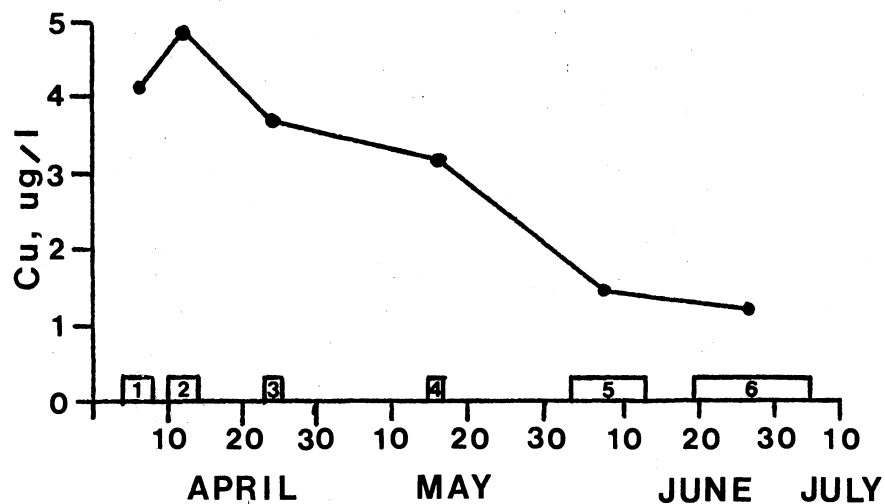


Figure 33. Mean Copper Concentration for Each Group of Sampling Dates After Rains Adjusted by Multiple Regression Analysis for Differences Between Stations and Among Days Following High Discharge

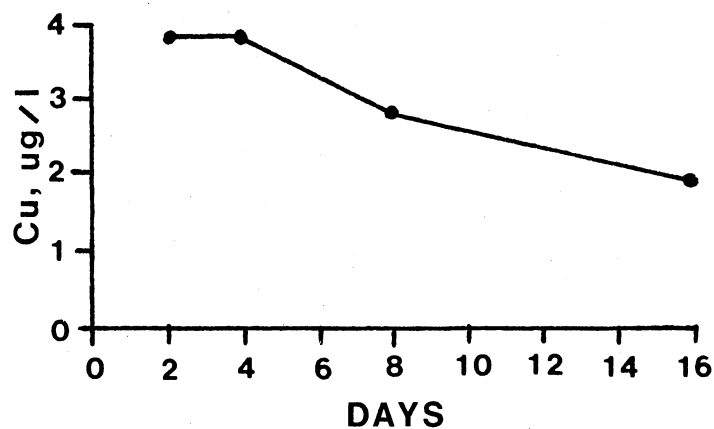


Figure 34. Mean Copper Concentration by Days After High Stream Discharge Adjusted by Multiple Regression Analysis for Differences Between Stations and Among Sampling Periods



existed at the 0.08 level. A decreasing amount of chromium entering Skeleton Creek from industrial wastes probably was responsible for the decline in chromium in the stream.

Concentration of chromium in Skeleton Creek decreased from 3.2  $\mu\text{g/l}$  at Day 2 to 1.6  $\mu\text{g/l}$  at Day 16 (Figure 36). Although differences among means were small and variability among sampling dates was high, the differences were significant at the 0.08 level. Smaller significance levels may have existed if more samples from Days 8 and 16 were available. The following linear regression of decrease in chromium with days after high discharge approached a logarithmic curve:

$$\log Y = 0.4593 - 0.0188 X$$

The coefficient was significantly different from zero at the 0.08 level.

No general trend existed for means of zinc concentrations in Skeleton Creek (Figure 37). The maximum mean of 10.9  $\mu\text{g/l}$  occurred after the April 9 rain and the minimum adjusted mean was -2.4  $\mu\text{g/l}$  after the May 1 rain. Differences among the means were not significant because of high variation among sampling dates in any one group of sampling dates. A decreasing concentration through the spring and summer months was expected because summer samples were much lower than winter samples (Figure 11).

A large reduction in zinc concentration occurred in Skeleton Creek during the first 8 days following the high stream discharge (Figure 38). The level was reduced from 10.2  $\mu\text{g/l}$  on Day 2 to 2.3  $\mu\text{g/l}$  on Day 16. However, differences among the means for days after high flow were not significant. High variation in zinc concentrations between the two sampling stations and among the different sampling dates probably was responsible for the absence of statistical significances. The following

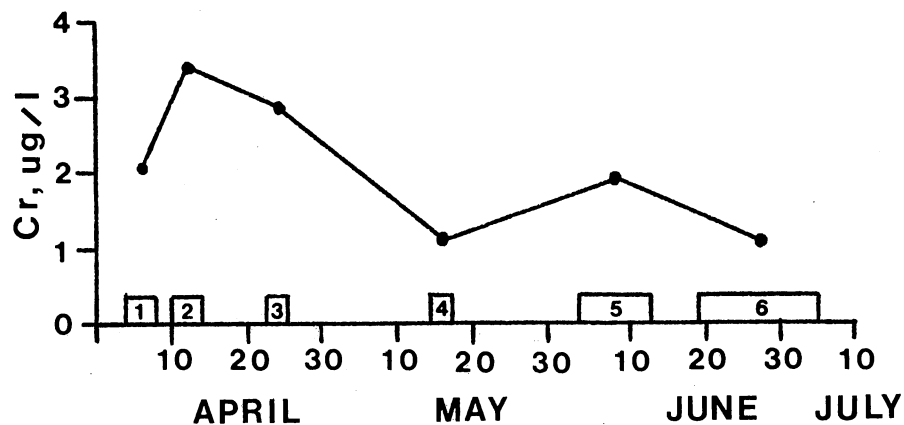


Figure 35. Mean Chromium Concentration for Each Group of Sampling Dates After Rains Adjusted by Multiple Regression Analysis for Differences Between Stations and Among Days Following High Discharge

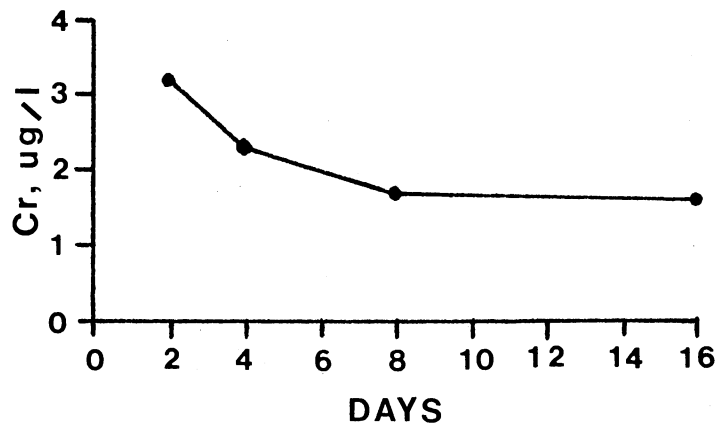


Figure 36. Mean Chromium Concentration by Days After High Stream Discharge Adjusted by Multiple Regression Analysis for Differences Between Stations and Among Sampling Periods

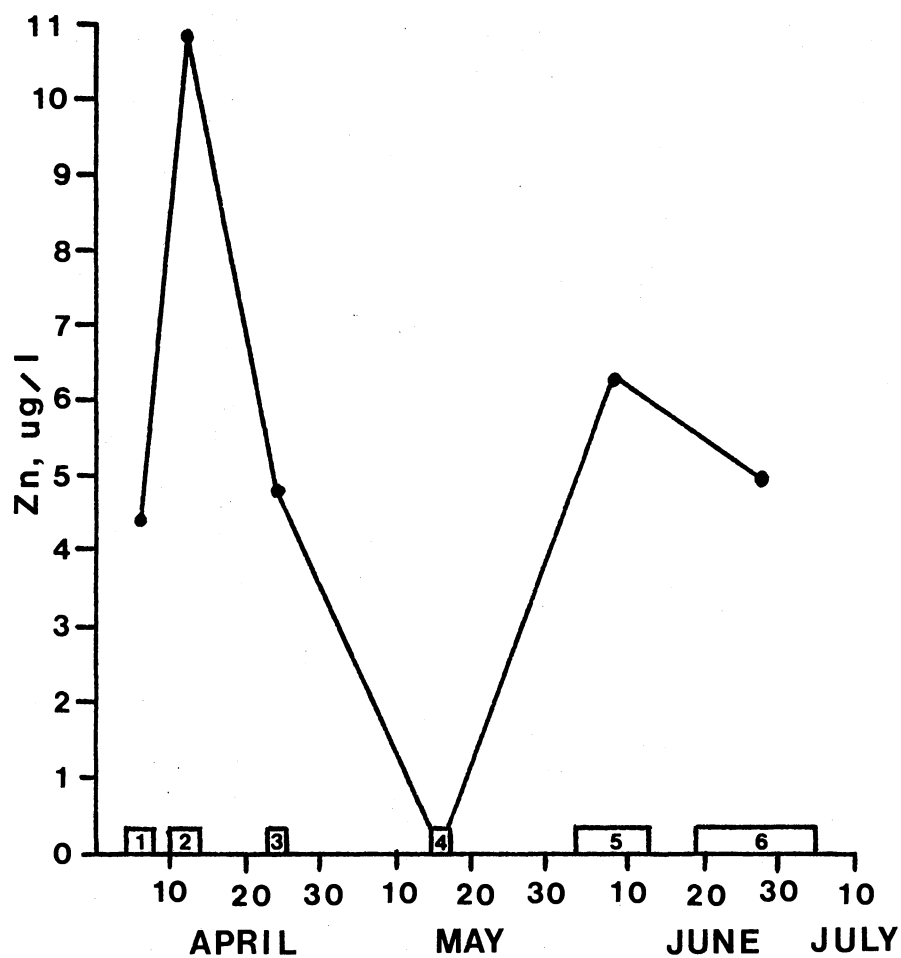


Figure 37. Mean Zinc Concentration for Each Group of Sampling Dates After Rains Adjusted by Multiple Regression Analysis for Differences Between Stations and Among Days Following High Discharge

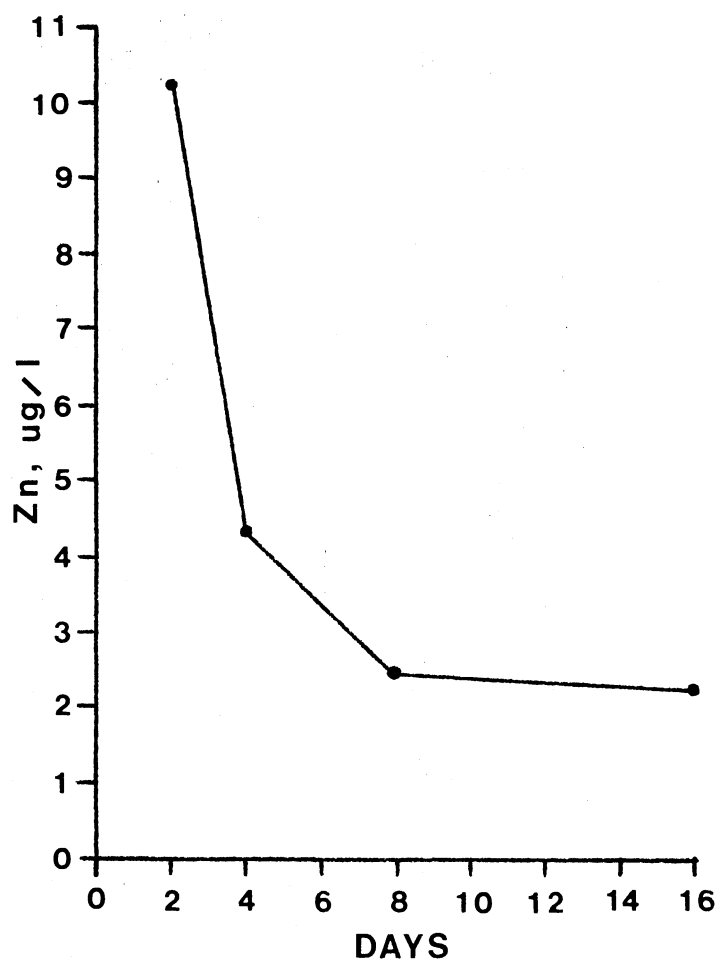


Figure 38. Mean Zinc Concentration by Days After High Stream Discharge Adjusted by Multiple Regression Analysis for Differences Between Stations and Among Sampling Periods

linear regression was used to see if the observed means fit a logarithmic equation:

$$\log Y = 0.8957 - 0.0396 X$$

The regression coefficient was different from zero at the 0.08 level.

Correlations between heavy metal concentrations and stream flow were not consistent. Measurements of heavy metals during low and high flow conditions showed that metals were positively correlated with discharge in one river and often were negatively correlated in another river (Durum and Haffty 1963). Although copper in suspended particulates coincided with high stream flow, other metals did not coincide in streams of the Cayuga Lake Basin, New York (Kubota et al. 1974).

Andelman (1973) concluded in a review article that no systematic correlation existed between metal concentrations and stream flow. Heavy metal concentrations increased rapidly with increased discharge and turbulence and quickly decreased following high stream discharge in the Ohio River, Ohio, and Black Warrior River, Alabama (Williams et al. 1966, 1973). Skeleton Creek data corresponded to the trend of decreased metals with time after high flow. Zinc concentration in the Ohio River at Cincinnati increased from 2 µg/l to over 19 µg/l and then decreased to less than 1 µg/l in 15 days during rapid changes in stream discharge. These fluctuations were attributed to resuspension of bottom particles during the increased turbulence. A positive correlation also existed between resuspended bottom sediments and heavy metal concentrations in the total water column of the Black Warrior River. However, no increase occurred in the metal levels in solution. The largest resuspension of bottom sediments occurred during high discharge and scouring from heavy rain runoff. A similar condition probably occurred

in Skeleton Creek because metal levels and turbidity decreased with time after high flow.

#### Copper, Chromium, Lead, and Zinc in Sediments

Little variation existed among means of copper, lead, and percent loss on ignition for the six sampling periods from April 4 through July 4 (Figure 39). Although chromium and zinc levels had larger variations, no differences among means for the sampling periods were significant. Increasing metal concentrations with time were expected because summer means were higher than winter means (Figures 12, 18, 22, and 25). Greater differences among the sampling periods probably were not present because Station 50 was not sampled for these analyses. Larger differences between winter and summer means occurred at Station 50 than at Stations 6 and 97.

Heavy metals in Skeleton Creek sediments had little variation in mean concentrations when values for specific days following high stream discharge of the various study periods were combined (Figure 40). Mean levels of copper and lead increased slightly with time after high flow. No trend was evident for chromium and zinc concentrations. Differences among means for each heavy metal for days after high stream discharge were not significant.

Minor fluctuations in the heavy metal content of Skeleton Creek sediments may be attributed to localized redistribution of sediments. Stream sediments are scoured and resuspended at higher discharge (Leopold et al. 1964). Heavy metals were associated with particulate material in the Ohio and Black Warrior Rivers, and metals were found in greater concentrations in suspended materials during high discharge

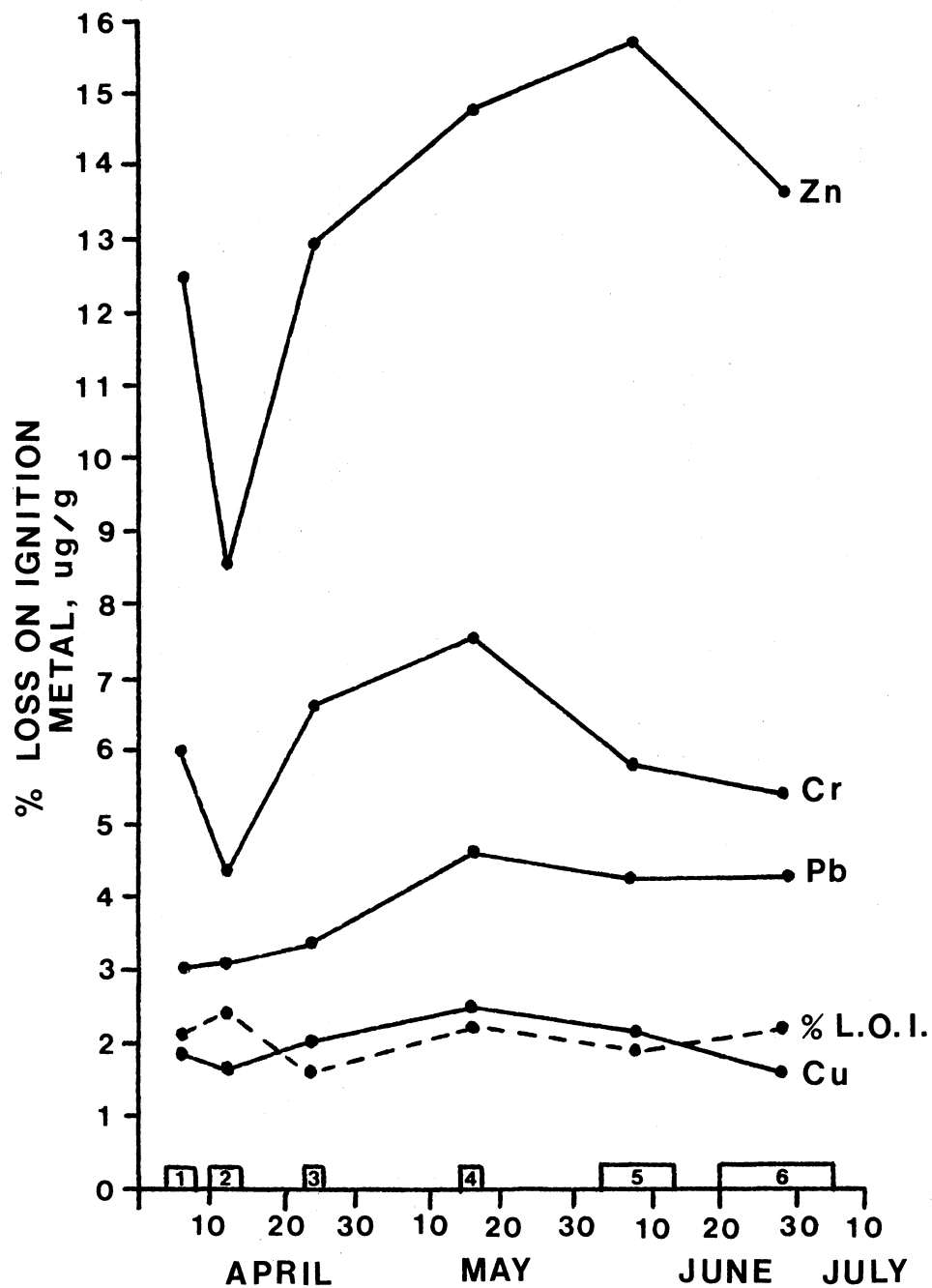


Figure 39. Means of Heavy Metal Concentrations and Percent Loss on Ignition by Sampling Periods After Rainfall Adjusted by Multiple Regression Analysis for Differences Between Stations and Among Days After High Stream Discharge

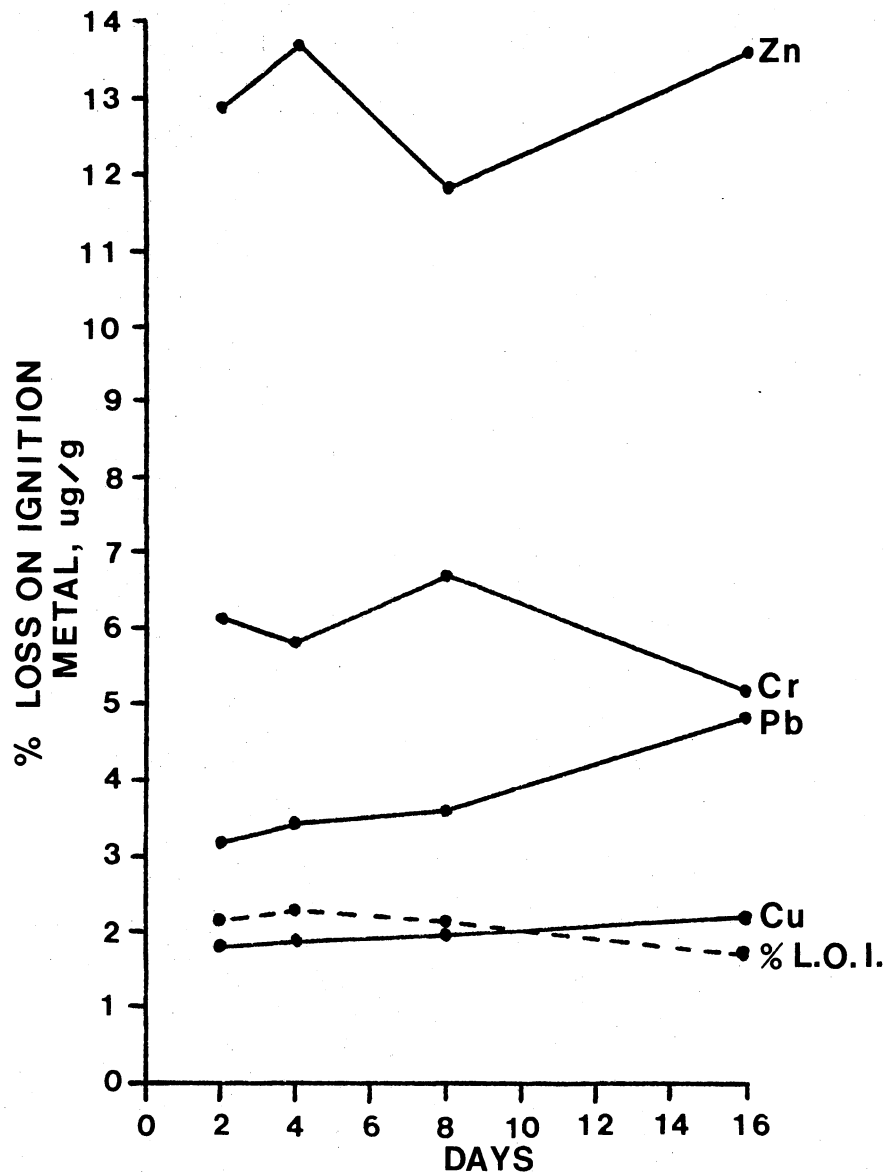


Figure 40. Means of Heavy Metal Concentrations and Percent Loss on Ignition by Days After High Stream Discharge Adjusted by Multiple Regression Analysis for Differences Between Stations and Among Sampling Periods



(Williams et al. 1966, 1973). Few investigators have reported changes in metal concentrations in stream sediments following high discharge. The processes of scouring and filling occur simultaneously in streams with a net loss of sediment downstream (Leopold et al. 1964).

Loss on ignition did not increase with time after high flow in Skeleton Creek sediments (Figure 40). In contrast, Ohio and Black Warrior River sediments accumulated organic material and heavy metals with time coinciding with low stream flow and sediment accumulation (Williams et al. 1966, 1973).

Heavy metals in sediments were found in higher concentrations after one of the worst floods in the history of Skeleton Creek (Figure 39). On October 10, 1973, a rainfall of 39.83 cm in 24 h resulted in a peak discharge on October 12 of 444.62 m<sup>3</sup>/sec at Kilometer 76. Means of the six sediment cores each collected on October 19 and 24 at Stations 6 and 97 are presented in Table IX. Sediment samples had higher heavy metal concentrations on October 19 than on October 24 at Station 6. However, differences between day means were not significant because of the high variation among the six cores on each date. In contrast, the Station 97 mean was significantly higher on October 24 than on October 19. Copper increased by 1.43 µg/g ( $0.01 < p < 0.02$ ), chromium by 2.40 µg/g ( $0.02 < p < 0.05$ ), lead by 2.18 µg/g ( $p = 0.08$ ), and zinc increased by 4.46 µg/g ( $p = 0.08$ ) from October 19 to October 25.

Higher heavy metal concentrations in sediments in October were believed to be due to scouring of oil refinery holding ponds during flooding and the deposition of suspended matter carrying the metals in Skeleton Creek sediments. Large patches of oily material were found along the shore and in the sediments on the October sampling dates.

Two cores from Station 6 on each sampling date had black oily residues included. Concentrations of copper, chromium, lead, and zinc were much higher in these cores (Table X). Percent loss on ignition was also higher for these cores.

TABLE IX  
MEANS AND STANDARD DEVIATIONS OF COPPER, CHROMIUM,  
LEAD, AND ZINC AFTER OCTOBER FLOOD, 1973

Dates	Stations	Metals ( $\mu\text{g/g}$ )			
		Cu	Cr	Pb	Zn
19 Oct 73	6	5.45 (6.41) <sup>a</sup>	10.03 (8.01)	11.21 (13.54)	27.17 (32.94)
	97	1.41 (0.48)	5.14 (1.26)	3.93 (1.34)	5.40 (1.86)
25 Oct 73	6	3.90 (4.45)	6.71 (3.55)	9.08 (8.63)	16.22 (12.85)
	97	2.84 (1.02)	7.54 (2.13)	6.11 (2.20)	9.86 (5.04)

<sup>a</sup>Standard deviations are in parentheses.

TABLE X  
MEANS FOR CORES CONTAINING OILY MATERIALS

Dates	Cores	Metals ( $\mu\text{g/g}$ )				Loss on Ignition (%)
		Cu	Cr	Pb	Zn	
19 Oct 73	1	9.06	10.36	16.23	29.78	3.85
	2	16.99	6.48	36.70	92.29	2.80
24 Oct 73	1	7.21	9.01	14.29	26.72	4.60
	2	11.37	10.66	23.68	36.11	3.05

## CHAPTER VIII

### CONDITIONS FOLLOWING REFINERY CLEANUP

#### Environmental Conditions

Environmental conditions in Skeleton Creek following refinery cleanup procedures were influenced by a total precipitation of 4.22 cm on May 23, 24, 25, 28, 30, 31, and June 2. Discharge gauged at Kilometer 76 exhibited an initial increase on May 31, a peak flow on June 3, and reduced flow on June 4. Mean water temperature ranged from 21.5 C on May 26 to 25.2 C on May 29 (Table XI). Dissolved oxygen increased from 6.4 mg/l on May 26 to 11.6 mg/l on May 29 (Table XI). The variation was attributed to sampling time, weather conditions, runoff, and fluctuations in municipal and industrial wastes. Little variation existed in pH among sampling dates except for the pH of 8.7 on May 29 (Table XI). Oil refinery effluents from the cleanup were expected to reach Skeleton Creek on May 27 (Mr. Bruce Hodgden, Champlin Oil Refinery, Enid, Oklahoma), and possibly caused the increased pH on May 29.

Alkalinity decreased from 281.5 mg/l on May 29 to 173.0 mg/l on June 4 (Figure 41). During this same period, turbidity increased from 79.5 JTU to 249.5 JTU. The reduced alkalinity and increased turbidity reflected increased runoff and dilution in Skeleton Creek as a result of precipitation.

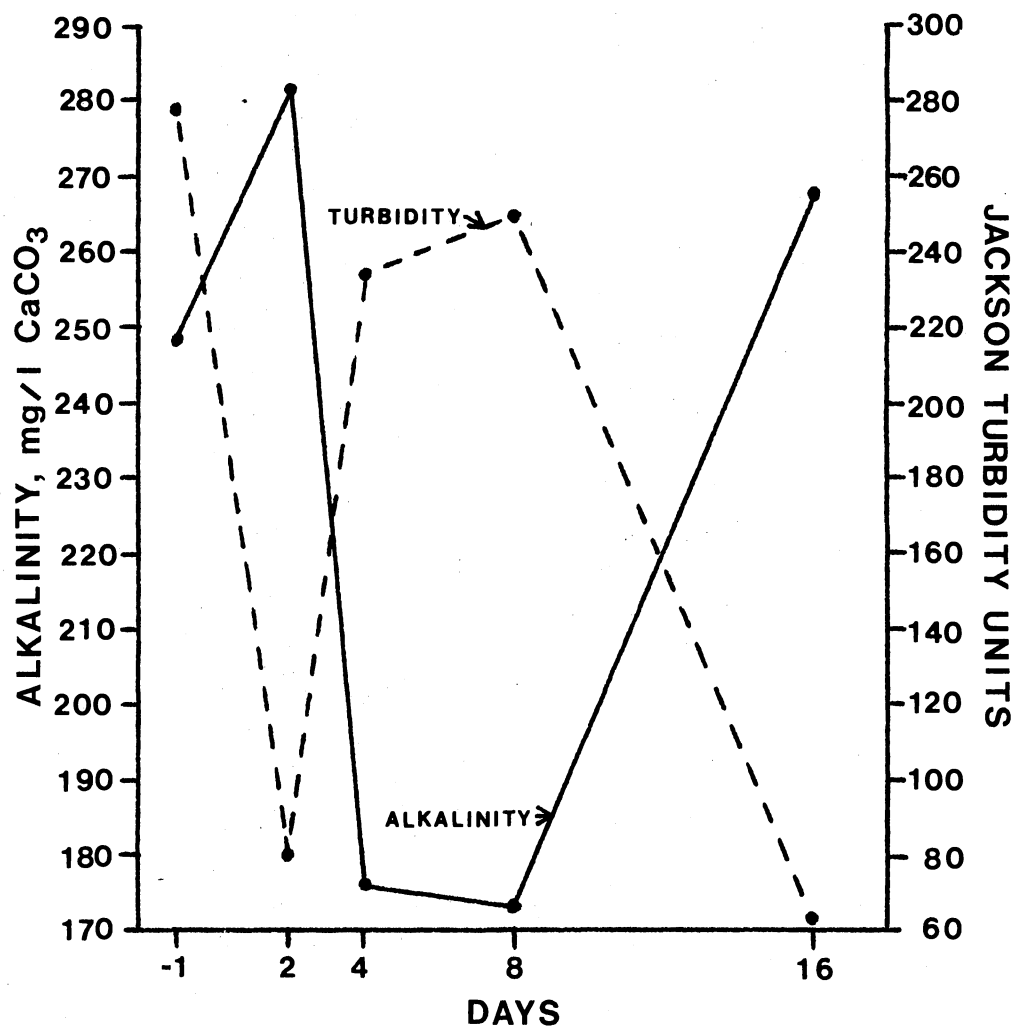


Figure 41. Mean Alkalinity and Turbidity by Sampling Dates Following Refinery Cleanup

TABLE XI  
MEAN WATER TEMPERATURE, DISSOLVED OXYGEN, AND pH

Dates	Temperature (C)	Dissolved Oxygen (mg/l)	pH
26 May 73	21.5	6.4	8.2
29 May 73	25.2	11.6	8.6
31 May 73	22.5	6.6	8.2
4 June 73	23.5	6.7	8.2
12 June 73	24.5	7.4	8.4

#### Copper, Chromium, Lead, and Zinc in Water

Copper concentration at Skeleton Creek Station 6 decreased from 9.2  $\mu\text{g/l}$  on Day -1 to 1.2  $\mu\text{g/l}$  on Day 16 (Figure 42). Station 97 copper level increased to 6.2  $\mu\text{g/l}$  on Day 2, then decreased to a nondetectable amount on Day 16. Differences among means of sampling dates were highly significant ( $p < 0.0005$ ); however, the results are complicated by concomitant increased runoff and discharge in Skeleton Creek.

Highest chromium concentrations were 3.8  $\mu\text{g/l}$  on Day 4 at Station 6 and 4.8  $\mu\text{g/l}$  on Day 8 at Station 97 (Figure 43). Lowest means occurred on Day 2 at both stations. Variation among sampling dates was highly significant ( $p < 0.0005$ ).

Lead in Skeleton Creek water averaged 24.0  $\mu\text{g/l}$  on Day 4 at Station 6 and 12.2  $\mu\text{g/l}$  on Day 8 at Station 97 (Figure 44). Because these were the only two means above detectable levels in the statistical analysis, differences among sampling dates were highly significant ( $p < 0.0005$ ).

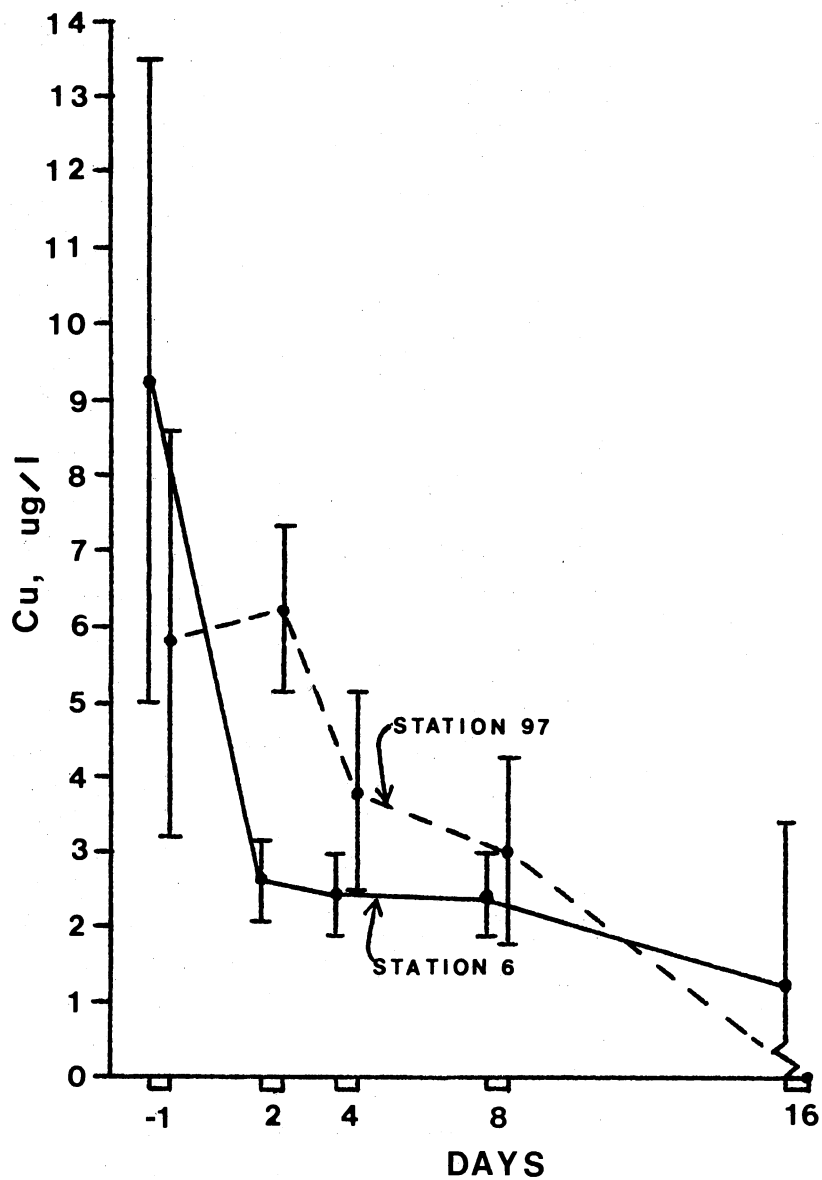


Figure 42. Mean Copper Concentration in Water  
± Standard Deviations for  
Sampling Dates Following  
Refinery Cleanup

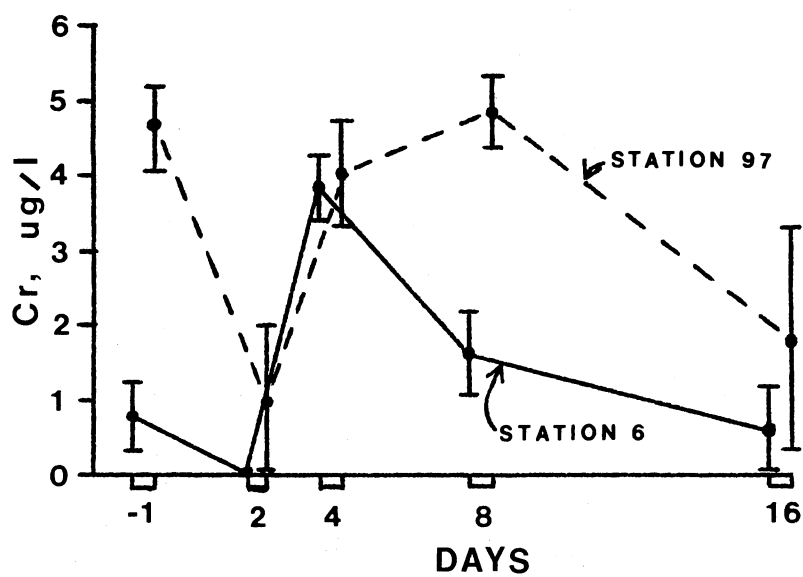


Figure 43. Mean Chromium Concentration in Water  $\pm$  Standard Deviations for Sampling Dates Following Refinery Cleanup



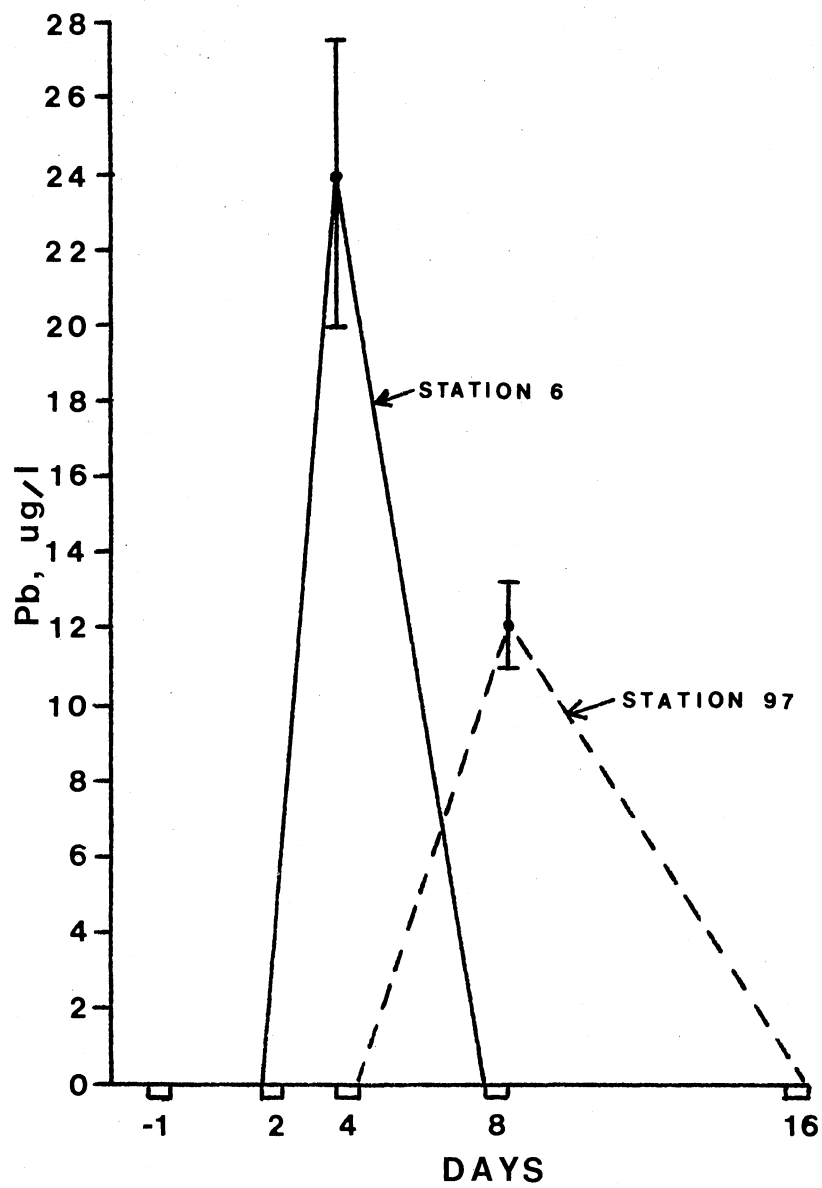


Figure 44. Mean Lead Concentration in Water + Standard Deviations for Sampling Dates Following Refinery Cleanup

Zinc concentration was highest on Day 4 at Station 6 and on Day 8 at Station 97 (Figure 45). Concentrations were 35.6 and 25.8  $\mu\text{g/l}$  for Stations 6 and 97, respectively. Like chromium and lead, variation of means among sampling dates was highly significant ( $p < 0.0005$ ).

Slug loads of chromium, lead, and zinc entered Skeleton Creek on approximately May 31 (Day 4). High concentrations of these metals were found 4 days later at Station 97 (Figures 43, 44, and 45). The date that effluents from oil refinery cleanup processes were expected to reach Skeleton Creek was estimated by the approximate time needed for wastes to pass through the water treatment facilities. The Day 0 estimate may have been in error and the actual date of discharge into Skeleton Creek may have been May 31 (Day 4). The source of these heavy metals could not be attributed solely to oil refinery wastes since runoff from Enid also may have affected the metal content of the water. High heavy metal concentrations ranked in decreasing order of abundance in street runoff were lead, zinc, chromium, and copper, respectively (Sartor and Boyd 1972; Pitt and Amy 1973). Street surfaces which had been flushed by a recent rain had lower metal concentrations in the runoff than runoff from streets without a recent flushing (Sartor and Boyd 1972). Enid streets had been flushed on three occasions a few days prior to the May 31 (Day 4) samples. Thus, slug loads of heavy metals observed in Skeleton Creek were not expected from runoff alone.

#### Copper, Chromium, Lead, and Zinc in Sediments

Changes in heavy metal concentrations similar to those found in water did not occur in the sediments of Skeleton Creek following oil refinery cleanup or following increased stream discharge from runoff in

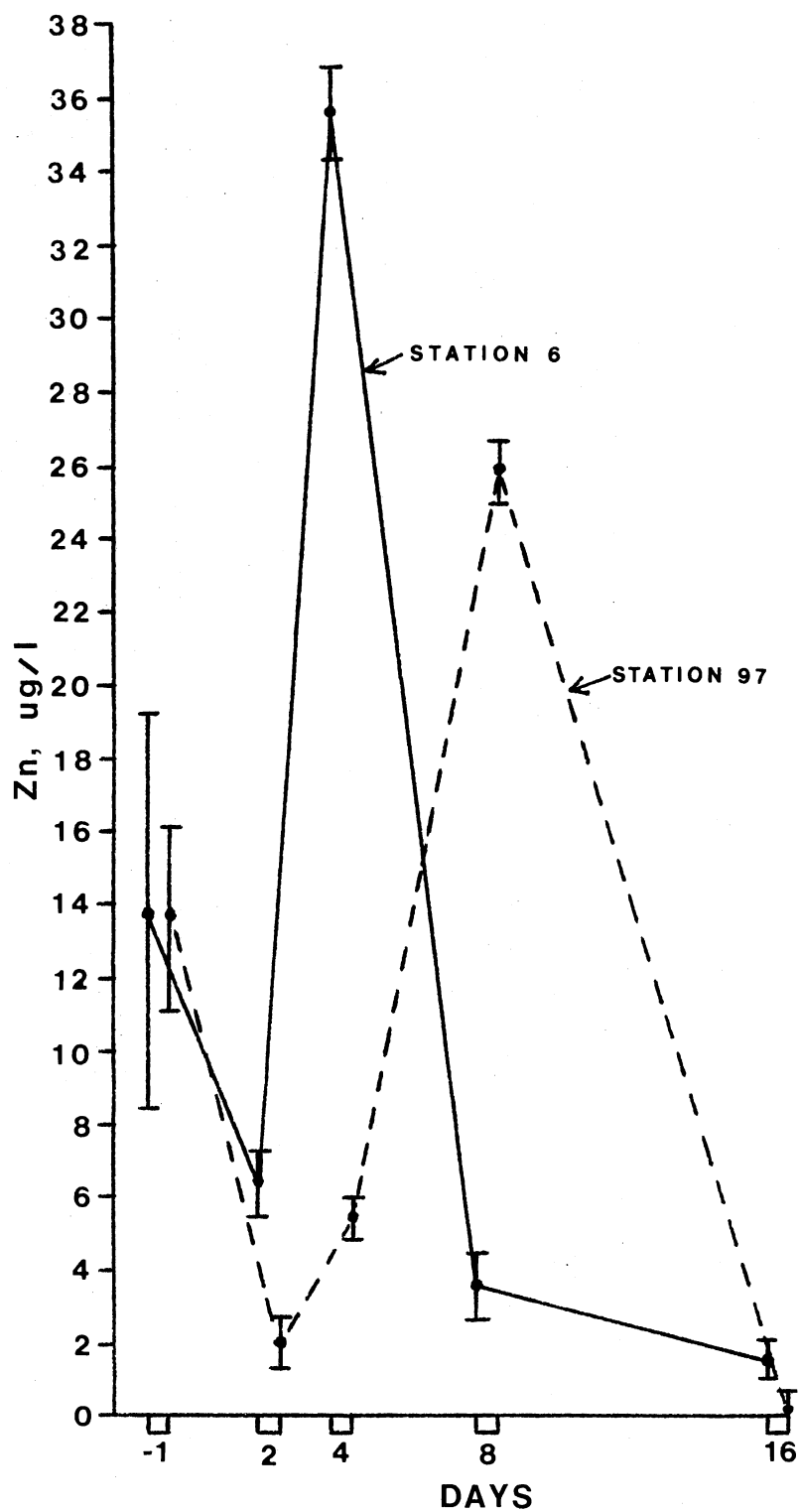


Figure 45. Mean Zinc Concentration in Water  $\pm$  Standard Deviations for Sampling Dates Following Refinery Cleanup

early June. No significant differences existed in heavy metal concentrations among the five means for days after high flow. Ranges for means of the heavy metals were 1.50 to 2.68  $\mu\text{g/g}$  for copper (Figure 46); 5.14 to 9.55  $\mu\text{g/g}$  for chromium (Figure 47); 2.72 to 5.31  $\mu\text{g/g}$  for lead (Figure 48); and 11.85 to 22.27  $\mu\text{g/g}$  for zinc (Figure 49).

Higher levels of heavy metals in Skeleton Creek water were not reflected by higher levels in the sediments possibly because the increased flow reduced the amount of metals that became associated with sediments. This probably occurred because metals were associated with the fine suspended particles which were not deposited on the stream bed during high discharge conditions.

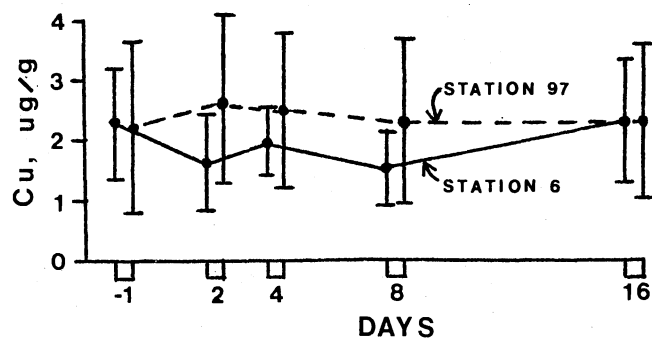


Figure 46. Mean Copper Concentration in Sediments  $\pm$  Standard Deviations for Sampling Dates Following Refinery Cleanup

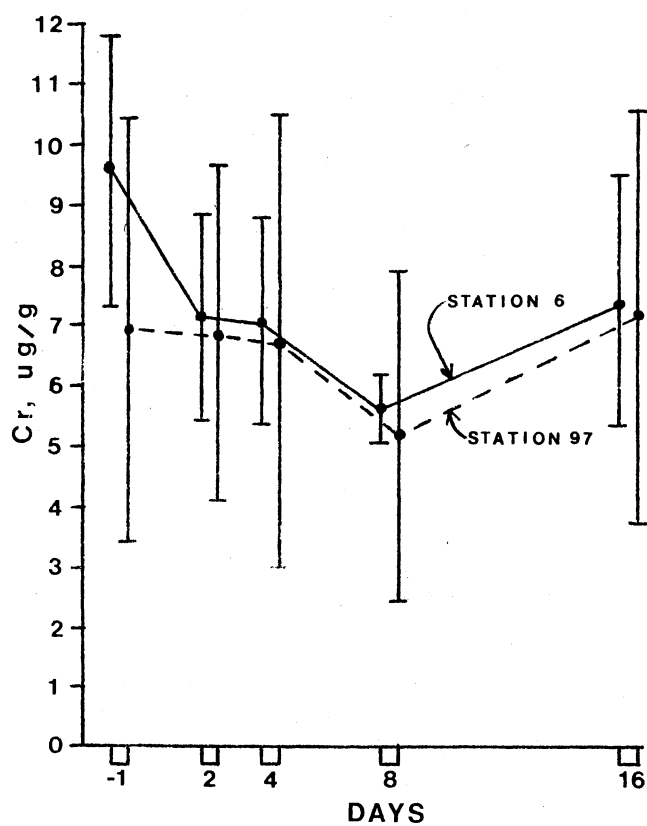


Figure 47. Mean Chromium Concentration in Sediments  $\pm$  Standard Deviations for Sampling Dates Following Refinery Cleanup

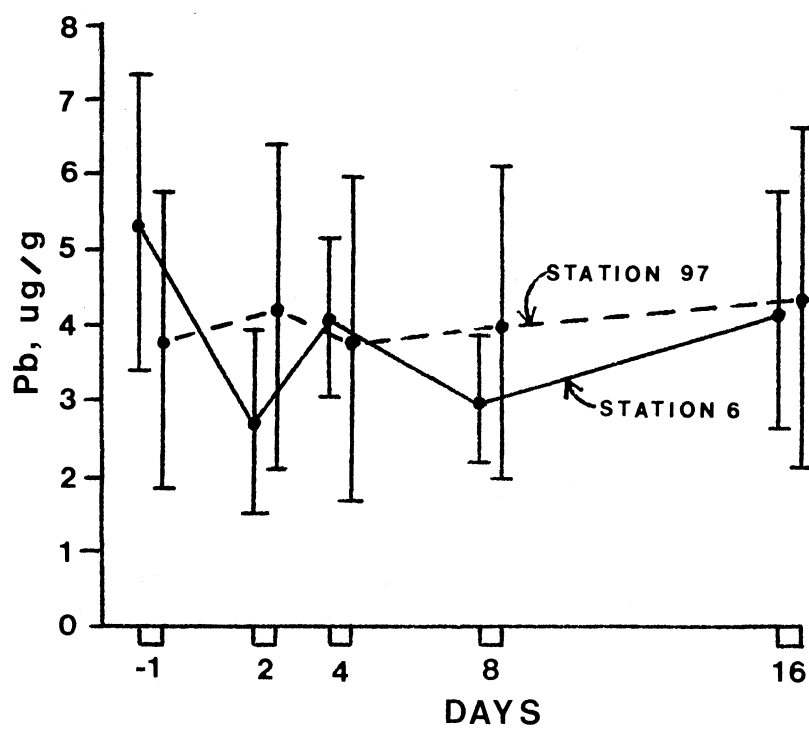


Figure 48. Mean Lead Concentration in Sediments  $\pm$  Standard Deviations for Sampling Dates Following Refinery Cleanup

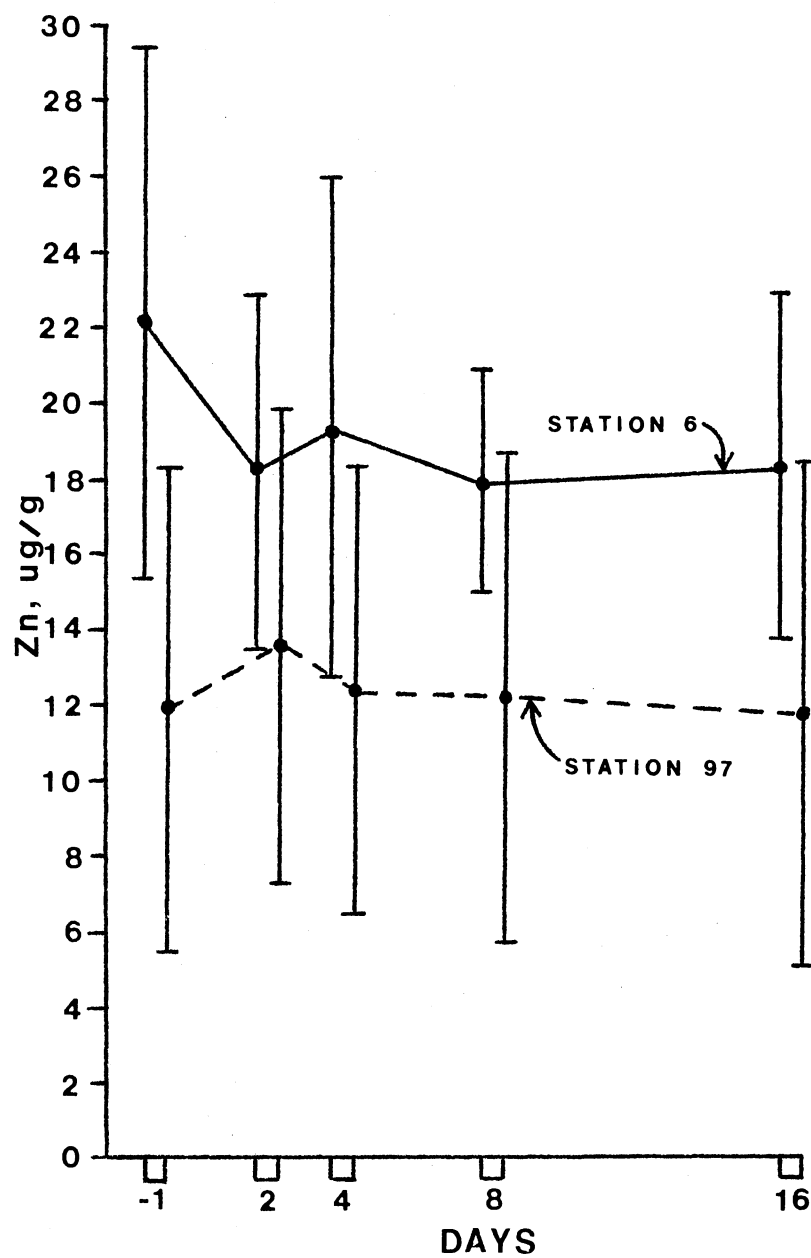


Figure 49. Mean Zinc Concentration in Sediments  
± Standard Deviations for Sampling  
Dates Following Refinery Cleanup

## CHAPTER IX

### SUMMARY

1. Distribution of copper, chromium, lead, and zinc in the water, sediments, and chironomids was studied at five stations in Skeleton Creek, Oklahoma, a stream receiving oil refinery and municipal sewage effluents, February through October, 1973.

2. Precision and accuracy were better for determinations made with flame atomic adsorption than those made with the heated graphite atomizer (HGA). Matrix interferences were large for zinc determinations made by the HGA which resulted in underestimating concentrations in water. Copper, lead, and zinc concentrations in sediment extracts were also underestimated due to matrix interference during flame atomic absorption.

3. Copper, chromium, and zinc concentrations in water were higher in winter than in summer, and highest concentrations generally occurred just below the outfall. Metals in sediments were generally higher in summer than in winter and highest concentrations occurred farther downstream. Warm water temperature and the concomitant increased microbial activity probably were responsible for higher levels in sediments in summer.

4. Organic matter and heavy metals in the sediments were related positively in summer but no relationship was evident in winter. The <0.5 mm particle size generally increased downstream and possibly affected the distribution of organic matter in Skeleton Creek.



5. Ammonium acetate extractions were ineffective in removing ion exchangeable metals from sediments indicating that heavy metals were not adsorbed on the surfaces.

6. Concentrations of heavy metals in chironomid larvae were two to three orders of magnitude greater than in the water but were comparable to levels in sediments.

7. Copper, chromium, and zinc concentrations in water generally decreased exponentially with time following high stream discharge. No significant trends existed in the distribution of heavy metals in sediments following high discharge. Heavy metal levels were higher in sediments after the October 10, 1973, flood than after high discharge during spring and summer. Metal concentrations were considerably higher in sediments containing oily residues than other sediments.

8. Copper concentration in water generally decreased following refinery cleanup while chromium, lead, and zinc exhibited peak concentrations 4 to 8 days after the date effluents from an oil refinery cleanup were expected to enter Skeleton Creek. No significant changes in heavy metal concentrations occurred in the sediments. The influence of an oil refinery cleanup operation on the distribution of heavy metals was obscured by concomitant increased flow from runoff.

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## APPENDIX

TABLE XII

CHROMIUM, COPPER, LEAD, AND ZINC IN WATER, SEDIMENTS,  
AND BIOTA REPORTED IN THE LITERATURE

Water ( $\mu\text{g}/\text{l}$ )	Sediments ( $\mu\text{g}/\text{g}$ )	Organisms ( $\mu\text{g}/\text{g}$ )	Locale	Source
<u>CHROMIUM</u>				
0.05	-	-	seawater	Goldberg (1957)
-	307	bivalves (10)	Tasman Bay, New Zealand	Brooks and Rumsby (1965)
26	-	-	St. Lawrence River, N.Y.	Kopp and Kroner (1968)
-	-	oysters <sup>a</sup> (0.4)	Atlantic coast	Pringle et al. (1968)
-	130 <sup>b</sup>	-	Experimental Lakes, Canada	Brunskill et al. (1971)
19	-	-	Irish Buffalo Creek, N.C.	Durum et al. (1971)
21	17	tubificids (9) clams (5.7)	Illinois River, Illinois	Mathis and Cummings (1971)
10	12	-	Mississippi River, Iowa	Morris et al. (1972)
<u>COPPER</u>				
3	-	-	seawater	Goldberg (1957)
-	-	zooplankton (325)	NE of US	Nicholls et al. (1959)
-	102	bivalves (19.7)	Tasman Bay, New Zealand	Brooks and Rumsby (1965)
1.2	-	-	High Sierra Lakes, Cal.	Bradford et al. (1968)
5.2	-	-	Minnesota	Bright (1968)
66	-	-	Monongahela River, Penn.	Kopp and Kroner (1968)

TABLE XII (Continued)

Water ( $\mu\text{g}/\text{l}$ )	Sediments ( $\mu\text{g}/\text{g}$ )	Organisms ( $\mu\text{g}/\text{g}$ )	Locale	Source
-	-	oysters <sup>a</sup> (91.50)	Atlantic coast	Pringle et al. (1968)
1.5	-	-	Lake Erie	Chawla and Chau (1969)
-	-	spottail shiner (1.2)	Lake Erie	Lucas et al. (1969)
-	-	zooplankton (41)	Puerto Rico	Martin (1970)
-	39	-	Lake Michigan	Shimp et al. (1970)
1.1	19	tubificids (24) clams (1.5)	Illinois River, Illinois	Mathis and Cummings (1971)
-	30	-	Lake Michigan	Shimp et al. (1971)
-	-	largemouth bass (6.2)	Savannah River	Goodyear and Boyd (1972)
10	10	-	Mississippi River, Iowa	Morris et al. (1972)
5	11.8	-	Lake Carl Blackwell, Okla.	Sias (1974)
5	51.4	benthos (234)	Theta Pond, Okla.	Namminga et al. (1974)
<u>LEAD</u>				
3	-	-	seawater	Goldberg (1957)
-	5	-	Tasman Bay, New Zealand	Brooks and Rumsby (1965)
0.5	-	-	High Sierra Lakes, Cal.	Bradford et al. (1968)
56	-	-	Ohio River, West Virginia	Kopp and Kroner (1968)

TABLE XII (Continued)

Water ( $\mu\text{g/l}$ )	Sediments ( $\mu\text{g/g}$ )	Organisms ( $\mu\text{g/g}$ )	Locale	Source
-	-	oysters <sup>a</sup> (0.47)	Atlantic coast	Pringle et al. (1968)
4	-	-	Lake Erie	Chawla and Chau (1969)
2	28	tubificids (18) clams (2.9)	Illinois River, Illinois	Mathis and Cummings (1971)
890	-	-	St. Croix River, Maine	Durum et al. (1971)
-	27	-	Lake Michigan	Shimp et al. (1970)
-	48	-	Lake Michigan	Shimp et al. (1971)
10	14	-	Mississippi River, Iowa	Morris et al. (1972)
3	25.0	-	Lake Carl Blackwell, Okla.	Sias (1974)
13	529.0	benthos (37)	Theta Pond, Okla.	Namminga et al. (1974)
<u>ZINC</u>				
116-332	-	-	Saale River, Germany	Heide and Singer (1954)
10	-	-	seawater	Goldberg (1957)
7	10-18	-	Redfish Bay, Texas	Parker (1962)
38	400	-	Potomac River, Md.	O'Connor et al. (1964)
116	398	-	Big Gunpowder Falls River, Md.	O'Connor et al. (1964)
1.5	-	-	High Sierra Lakes, Cal.	Bradford et al. (1968)

TABLE XII (Continued)

Water ( $\mu\text{g/l}$ )	Sediments ( $\mu\text{g/g}$ )	Organisms ( $\mu\text{g/g}$ )	Locale	Source
8	-	-	Lake Erie	Chawla and Chau (1969)
0.6	8.7	polychaetes (79)	Newport River Estuary, Md.	Cross et al. (1970)
-	-	zooplankton (426)	Puerto Rico	Martin (1970)
-	84	-	Lake Michigan	Shimp et al. (1970)
-	70 <sup>b</sup>	-	Experimental Lakes, Canada	Brunskill et al. (1971)
42,000	-	-	Mineral Creek, Arizona	Durum et al. (1971)
31	81	tubificids (40) clams (95)	Illinois River, Illinois	Mathis and Cummings (1971)
-	119	-	Lake Michigan	Shimp et al. (1971)
-	-	largemouth bass (48.5)	Savannah River	Goodyear and Boyd (1972)
10	79	-	Mississippi River, Iowa	Morris et al. (1972)
20	42.1	-	Lake Carl Blackwell	Sias (1974)
16	219.6	benthos (410)	Theta Pond, Okla.	Namminga et al. (1974)

(a) by wet weight

(b) by ash weight

(-) no record

TABLE XIII  
MEANS AND DIFFERENCES FOR COPPER IN WATER  
BY STATION IN WINTER<sup>a</sup>

Station means ( $\mu\text{g/l}$ )	Station number	Differences				
		-8	97	50	24	6
2.9	-8	0	0.3	2.4	3.6	11.0 <sup>b</sup>
3.2	97		0	2.1	3.3	10.7 <sup>b</sup>
5.3	50			0	1.2	8.6 <sup>b</sup>
6.5	24				0	7.4 <sup>b</sup>
13.9	6					0

<sup>a</sup>Differences are obtained by subtracting the mean of the row stations from the mean of the column stations.

<sup>b</sup>Differences larger than  $\text{LSD}_{0.05} = 5.4$  are significant.

TABLE XIV  
MEANS AND DIFFERENCES FOR ZINC IN WATER  
BY STATION IN WINTER<sup>a</sup>

Station means ( $\mu\text{g/l}$ )	Station number	Differences				
		-8	97	50	24	6
6.7	-8	0	3.3	8.1	21.1 <sup>b</sup>	24.2 <sup>b</sup>
10.0	97		0	4.8	17.8 <sup>b</sup>	21.1 <sup>b</sup>
14.8	50			0	13.0	16.3 <sup>b</sup>
27.8	24				0	3.3
31.1	6					0

<sup>a</sup>Differences are obtained by subtracting the mean of the row stations from the mean of the column stations.

<sup>b</sup>Differences larger than  $\text{LSD}_{0.05} = 13.6$  are significant.

TABLE XV  
MEANS AND DIFFERENCES FOR COPPER IN SEDIMENTS  
BY STATION AND SEASON<sup>a</sup>

Station means (μg/g)	Station number	Differences				
<u>WINTER</u>						
		6	-8	97	24	50
0.34	6	0	0.05	0.76	1.25 <sup>b</sup>	1.52 <sup>b</sup>
0.39	-8		0	0.71	1.20 <sup>b</sup>	1.47 <sup>b</sup>
1.10	97			0	0.49	0.76
1.59	24				0	0.27
1.86	50					0
<u>SUMMER</u>						
		-8	97	24	6	50
1.32	-8	0	0.21	0.38	0.45	5.08 <sup>b</sup>
1.53	97		0	0.17	0.24	4.87 <sup>b</sup>
1.70	24			0	0.07	4.70 <sup>b</sup>
1.77	6				0	4.63 <sup>b</sup>
6.40	50					0

<sup>a</sup>Differences are obtained by subtracting the mean of the row stations from the mean of the column stations.

<sup>b</sup>Differences larger than  $\text{LSD}_{0.05} = 1.18$  are significant.

TABLE XVI  
MEANS AND DIFFERENCES FOR PERCENT LOSS ON IGNITION  
IN SEDIMENTS BY STATION AND SEASON<sup>a</sup>

Station means %	Station number	Differences				
<u>WINTER</u>						
		-8	97	6	24	50
0.49	-8	0	2.52 <sup>b</sup>	2.70 <sup>b</sup>	2.87 <sup>b</sup>	3.30 <sup>b</sup>
3.01	97		0	0.18	0.35	0.78
3.19	6			0	0.17	0.60
3.36	24				0	0.43
3.79	50					0
<u>SUMMER</u>						
		-8	97	6	24	50
0.38	-8	0	1.45	1.92	1.97	4.77 <sup>b</sup>
1.83	97		0	0.47	0.52	3.32 <sup>b</sup>
2.30	6			0	0.05	2.85 <sup>b</sup>
2.35	24				0	2.80 <sup>b</sup>
5.15	50					0

<sup>a</sup>Differences are obtained by subtracting the mean of the row stations from the mean of the column stations.

<sup>b</sup>Differences larger than  $LSD_{0.05} = 2.38$  are significant.



TABLE XVII  
MEANS AND DIFFERENCES FOR <0.5 MM FRACTION PARTICLE  
SIZE OF SEDIMENTS BY STATION AND SEASON<sup>a</sup>

Station means %	Station number	Differences				
<u>WINTER</u>						
		6	-8	24	50	97
6.01	6	0	39.60 <sup>b</sup>	43.64 <sup>b</sup>	77.11 <sup>b</sup>	92.52 <sup>b</sup>
45.61	-8		0	4.04	37.51 <sup>b</sup>	52.92 <sup>b</sup>
49.65	24			0	33.47 <sup>b</sup>	48.88 <sup>b</sup>
83.12	50				0	15.41 <sup>b</sup>
98.53	97					0
<u>SUMMER</u>						
		6	-8	24	97	50
10.04	6	0	19.96 <sup>b</sup>	26.59 <sup>b</sup>	78.56 <sup>b</sup>	83.57 <sup>b</sup>
30.00	-8		0	6.63	58.60 <sup>b</sup>	63.61 <sup>b</sup>
36.63	24			0	51.97 <sup>b</sup>	56.98 <sup>b</sup>
88.60	97				0	5.01
93.61	50					0

<sup>a</sup>Differences are obtained by subtracting the mean of the row stations from the mean of the column stations.

<sup>b</sup>Differences larger than  $LSD_{0.05} = 12.24$  are significant.

TABLE XVIII  
MEANS AND DIFFERENCES FOR CHROMIUM IN SEDIMENTS  
BY STATION AND SEASON<sup>a</sup>

Station means (µg/g)	Station number	Differences				
<u>WINTER</u>						
		-8	6	24	97	50
1.32	-8	0	0.56	1.60	2.39 <sup>b</sup>	4.96 <sup>b</sup>
1.88	6		0	1.04	1.83 <sup>b</sup>	4.40 <sup>b</sup>
2.92	24			0	0.79	3.36 <sup>b</sup>
3.71	97				0	2.57 <sup>b</sup>
6.28	50					0
<u>SUMMER</u>						
		-8	97	24	6	50
2.40	-8	0	2.26 <sup>b</sup>	3.56 <sup>b</sup>	5.24 <sup>b</sup>	12.29 <sup>b</sup>
4.66	97		0	1.30	2.98 <sup>b</sup>	10.03 <sup>b</sup>
5.96	24			0	1.68 <sup>b</sup>	8.73 <sup>b</sup>
7.64	6				0	7.05 <sup>b</sup>
14.69	50					0

<sup>a</sup>Differences are obtained by subtracting the mean of the row stations from the mean of the column stations.

<sup>b</sup>Differences larger than  $\text{LSD}_{0.05} = 1.66$  are significant.

TABLE XIX  
MEANS AND DIFFERENCES FOR LEAD IN SEDIMENTS  
BY STATION AND SEASON<sup>a</sup>

Station means ( $\mu\text{g/g}$ )	Station number	Differences				
<u>WINTER</u>						
		6	-8	97	24	50
1.02	6	0	0.17	2.08 <sup>b</sup>	2.60 <sup>b</sup>	5.19 <sup>b</sup>
1.19	-8		0	1.91	2.43 <sup>b</sup>	5.02 <sup>b</sup>
3.10	97			0	0.52	3.11 <sup>b</sup>
3.61	24				0	2.59 <sup>b</sup>
6.21	50					0
<u>SUMMER</u>						
		-8	97	24	6	50
0.98	-8	0	1.76	2.08 <sup>b</sup>	2.36 <sup>b</sup>	9.16 <sup>b</sup>
2.74	97		0	0.32	0.60	7.40 <sup>b</sup>
3.06	24			0	0.28	7.08 <sup>b</sup>
3.34	6				0	6.80 <sup>b</sup>
10.14	50					0

<sup>a</sup>Differences are obtained by subtracting the mean of the row stations from the mean of the column stations.

<sup>b</sup>Differences larger than  $\text{LSD}_{0.05} = 2.00$  are significant.

TABLE XX  
MEANS AND DIFFERENCES FOR ZINC IN SEDIMENTS  
BY STATION AND SEASON<sup>a</sup>

Station means (μg/g)	Station number	Differences				
<u>WINTER</u>						
		-8	97	24	6	50
2.21	-8	0	1.50	5.34 <sup>b</sup>	5.43 <sup>b</sup>	6.99 <sup>b</sup>
3.71	97		0	3.84 <sup>b</sup>	3.93 <sup>b</sup>	5.49 <sup>b</sup>
7.55	24			0	0.09	1.65
7.64	6				0	1.56
9.20	50					0
<u>SUMMER</u>						
		-8	97	24	6	50
2.27	-8	0	3.86 <sup>b</sup>	8.59 <sup>b</sup>	13.73 <sup>b</sup>	24.33 <sup>b</sup>
6.13	97		0	4.73 <sup>b</sup>	9.87 <sup>b</sup>	20.47 <sup>b</sup>
10.86	24			0	5.14 <sup>b</sup>	15.74 <sup>b</sup>
16.00	6				0	10.60 <sup>b</sup>
26.60	50					0

<sup>a</sup>Differences are obtained by subtracting the mean of the row stations from the mean of the column stations.

<sup>b</sup>Differences larger than  $\text{LSD}_{0.05} = 2.28$  are significant.

VITA

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