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A GEOCHEMICAL STUDY OF TRACE METALS IN SEDIMENT FROM A FLUVIAL SYSTEM HEAVILY INFLUENCED BY THE MINING OF COAL

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee

Edward L. Schrader, Jr.

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ABSTRACT

The concentration, distribution and mode of occurrence of trace metals in sediment from the Indian Fork and New River fluvial systems was investigated and delineated. The sampling area was located in the southeastern quarter of the Fork Mountain quadrangle in northeastern Tennessee. The area was chosen due to its proximity to strip and deep mined highlands. This research produced the first reported data on trace metals in contemporary stream sediments affected by coal mining on the Cumberland Plateau of Tennessee.

Nine samples were taken. Sample material <1 mm was analyzed for concentrations of Cr, Co, Cu, Cd, Ni, Pb, Zn, Mn, and Fe. Size fractionation was carried out on portion of all samples and these fractions were analyzed for concentrations of the same metals.

A preliminary x-ray diffraction examination of the sediment was carried out. The major minerals comprising the sediment, in the area of study, were found to be quartz, illite, kaolinite, "soil montmorillonite" and "soil chlorite."

Certain metals travel not only as ions attached to sediment but also as cations sorbed onto hydrous metal oxides which may be suspended in the stream waters. Iron and Mn were found to be the dominant cations comprising these hydrous oxides. Trace metals were generally concentrated in clay and very fine silt-sized sediment fractions.

Elevation in total metal values was evident in sediments near the influx into a major stream of certain tributaries which were affected by coal mining. This elevation was found to be due to increased amounts of finer sediments, or enrichment of all sediments in metals carried by the tributary, or both processes acting simultaneously.

PREFACE



View of Indian Fork Near Its Headwaters.

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CHAPTER I

INTRODUCTION

I. PURPOSE AND SCOPE

As a result of strip mining, large amounts of coal and its enclosing strata become exposed to the atmosphere. Weathering of this material liberates a number of trace metals that may be ultimately incorporated in the fluvial system which drains the affected area. Once in the fluvial system, these metals may become available to biota. Thus, a potential health hazard may occur as a result of the initial mining.

The purpose of this research was to establish trends in the accumulation of trace metals in sediment from a fluvial system that is heavily affected by the surface mining of coal. This study delineated the total concentrations of certain trace metals at each sampling site, and the concentrations of metals within the constituent size fractions from each sample locality. A preliminary determination of the mineralogy of the sediments was accomplished. A relation between the presence of certain minerals and elevated metal concentrations has been suggested.

The nature of the hydrous Fe and Mn oxides was difficult to ascertain. Hereafter in the text the term "hydrous Fe oxides" (or Mn oxides) shall refer to any Fe (or Mn) oxide, hydroxide, or oxyhydroxide and their hydrated forms.

II. LOCATION

Because of the extensive strip and deep mining of coal in the northern Cumberland Plateau of Tennessee, this area was selected for study. The Indian Fork stream system, a tributary of the New River, and the section of New River directly affected by the addition of material from Indian Fork were designated the sampling area. The basins which these streams occupy were completely surrounded by strip mined highlands.

The sampling area is located in the southeast quarter of the Fork Mountain quadrangle, Figure 1. The coordinates of the center of this quadrangle are 84°25" west longitude and 36°10" north latitude. The area of interest is about 0.4 of a mile southeast of the junction between Scott, Anderson, and Morgan counties in northeastern Tennessee.

III. GEOLOGIC SETTING

The Cumberland Plateau of Tennessee is a long narrow arch between the coal basins of the central Appalachians to the north and the Black Warrior structural basin to the south. The portion of the plateau north of Interstate 40 is designated the northern Cumberland Plateau, and the area south of Interstate 40 is the southern Cumberland Plateau. In the coal basins Mississippian limestone underlies a thick sequence of sandstones and shales, of Pennsylvanian age (Milici, 1974).

The stratigraphic units which comprise the ridge forming strata are generally the Cross Mountain, Vowell Mountain, and Redoak

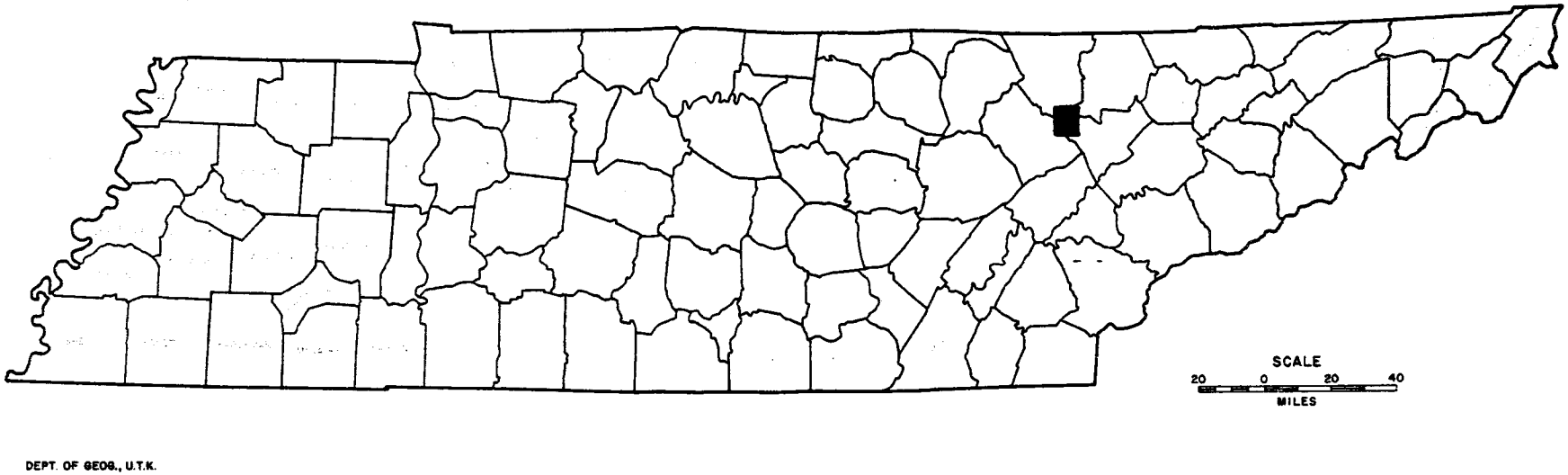


Figure 1. Outline map of Tennessee showing location of Fork Mountain Quadrangle.

Formations. Laterally-extensive and vertically-thick sand bodies within these formations usually cap the ridges in this region. The New River and Indian Fork channels are cut into the predominantly shaley Slatestone Formation. All of the above mentioned units are of Middle Pennsylvanian age (Luther and Avery, 1970).

The strata which surround the Indian Fork and New River fluvial systems are predominantly intercalated shales and sandstones with interspersed coal seams. A few thin-bedded limestones have been noticed in the Pennsylvanian sequence of the northern Cumberland Plateau by Dr. Kenneth Walker, Department of Geological Sciences, University of Tennessee at Knoxville (1975, personal communication). These limestones were not observed in the region of this study. All of the strata in this area are essentially horizontal.

CHAPTER II

REVIEW OF RELATED INVESTIGATIONS AND THEIR BEARING ON THE CURRENT STUDY

Due to an increased interest in environmental research, the results of many projects dealing with trace contaminants have been published. In spite of this fact, few of these projects have born a direct relation to the research set forth in this thesis. The following comments on background literature are therefore supportive in nature rather than correlative with the present research.

Ebens and Conner (1972) reported average concentrations of certain elements in Carboniferous strata. Since the stream sediment studied here was derived from the weathering of Pennsylvanian outcrops, some of the average concentrations reported by the above authors were helpful in understanding the sources of certain trace metals studied in the present research. Ebens and Conner (1972) presented the following data in µg/g:

Metal	Pennsylvanian Shales	Pennsylvanian Sandstones
Cr	95	33
Cu	23	8.4
Ni	38	19

Certain metal concentrations determined in this thesis approximate these values. Considering the above data it is possible that direct weathering and transport of these elements have occurred in the Indian Fork and New River drainage basins. Values for all other

metals studied in Ebens' and Conner's paper were lower than corresponding metal values presented in the present work.

Ebens and Conner (1972) also stated that Mn values with an average of 840 μg/g were common in Carboniferous limestones and Pb values averaging 44 μg/g were found in residuum from these same limestones. These concentrations could represent metal levels in the limestones on the northern Cumberland Plateau of Tennessee; however, since outcroppings of limestones are scarce in this region, it is not probable that this type of sedimentary rock provides significant quantities of metals to the studied area.

Crecelius, Bothner, and Carpenter (1975) performed "selective extraction" experiments on sediments from Puget Sound, Washington. The extractions were designed to determine a possible relationship between As and Sb and amorphous (hydrous) iron oxides. Citrate-dithionite-bicarbonate extractions removed about 33% of the total As and Sb. Although As and Sb were not included in the current study, similar extractions were carried out for other trace metals.

In recent years the suggestion has been made that elevated C and trace metal accumulations are concurrent phenomena. Frye and Shimp (1973) stated that although carbon concentrations as high as 6% were recorded, no consistent correlation between trace elements and carbon was found to occur. They felt that previously observed affinities of trace metals for organic carbon were due to man's influence on the drainage basin studied and not due to natural processes. The authors furthermore stated that man has strongly

influenced the trace metal content of sediments in their region of study. The relationship between carbon and trace metals was not explored in the present research.

The average crustal percentage of Cd, the Clarke value, was reported by Ruch, Gluskoter, and Shimp (1974) as 0.2 ppm. The same authors reported an average Cd concentration in coals from the Illinois Basin as 2.89 ppm. They reported that this relationship constitutes an enrichment factor of 14.4 of Cd in coals over the average crustal abundance. The conjecture arises that perhaps the coals in the Cumberland Plateau are a major source for Cd in stream sediment. Thus, increased strip mining would mean increased content of Cd in the affected drainage basin. However, Ruch, Gluskoter, and Shimp (1974) also reported concentrations of other metals in coals which were far below the metal values in the sediment obtained from the present research. Coal is probably not the major source for trace metals other than Cd.

Magee, Hall, and Varga (1973) reported that previously recorded values of trace elements associated with coals may be incorrect. Data obtained from analyses of weathered samples from surface outcrops may not be indicative of trace element concentrations in the coal at depth. The authors suggested that surface oxidation creates active sites on the coal with which trace elements in ground and flowing water can selectively react.

In a report from the Appalachian Regional Commission (1969) a chemical explanation of acid mine drainage was presented as follows:

1. $2FeS_2 + 7O_2 + 2H_2O \rightarrow 2FeSO_4 + 2H_2SO_4$;

2. $4FeSO_4 + O_2 + 2H_2SO_4 \rightarrow 2Fe_2(SO_4)_3 + 2H_2O$;

3. $Fe_2(SO_4)_3 + 6H_2O \rightarrow 2Fe(OH)_3 + 3H_2SO_4$.

The authors proposed that the acidity in mine waters is derived in the above stepwise manner. They further stated that natural neutralization of these waters may occur by reaction of the sulfuric acid with calcareous rock, either a limestone, calcareous siltstone, or calcareous shale. This neutralization can be presented as:

$$H_2SO_4 + CaCO_3 \rightarrow CaSO_4 + CO_2 + H_2O \quad .$$

Carbon dioxide formed during the above reaction plays an additional role in determining the alkalinity (or acidity) of mine waters by the formation of H_2CO_3 when that CO_2 is dissolved in water. This H_2CO_3 may then react with the remaining strata in the following manner:

$$H_2CO_3 + CaCO_3 \rightarrow Ca(HCO_3)_2 \quad .$$

When mine drainage of this nature reaches the surface, it does not become more acidic upon aeration (Appalachian Regional Commission, 1969).

The akalinity of mine drainage is directly dependent on the water volume and depth of the mine because these factors determine the amount of CO_2 in solution. Water in underground mines also has an opportunity to increase in alkalinity through reaction with basic

minerals in the mine walls and surrounding strata (Appalachian Regional Commission, 1969). Water pH values from the present study are presented in Table 24 in the Appendix.

According to Massey (1972), pH values near 6.0 caused precipitation of Zn, Ni, and Cu hydroxides from interstitial solutions in strip-mine spoil banks. Thus, these metals may be contributed to an affected fluvial system directly from mine products in the form of hydroxides.

Massey and Barnhisel (1972) reported that some metal values in unfiltered interstitial solution in strip-mine spoil banks have the following maxima (in ppm):

Fe	Mn	Zn	Cu	Ni
37,500	1800	145	85	122

These values approximate some of the metal concentrations reported in sediment analyzed in the current study. Thus, spoil bank material could be a major contributor to the heavy metal content of proximal fluvial systems.

Krauskopf (1956) stated that adsorption of cations increases with increasing surface area of adsorbent and increasing pH. Copper, Zn, and Pb were said to be more strongly and consistently adsorbed by clay minerals than other trace metals in natural waters. He also stated that Co and Ni, although likewise divalent cations, are much less effectively adsorbed.

Lockwood and Chen (1973) stated that adsorption of various metals can be very efficiently localized by Mn and Fe oxides. The adsorption

of unhydrolyzed cations on MnO_2 was attributed to ion exchange on the surface of the precipitated Mn material. Of various adsorbing oxides Mn was found to be by far the most effective and one of the most common in natural environments.

Colloidal MnO_2 (resulting from the aqueous solution of the dioxide) is actually a hydrous complex of indefinite structure and composition according to Posselt, Anderson, and Weber (1968). The complex can be written either as $MnO_{(1+x)} \cdot nH_2O$, or as $Mn(OH)_{(1+x)}$. The values for x in both cases may range from 0.1 to 0.95. The authors also stated that the surface charge on colloidal MnO_2 is largely determined by the pH of the solution. The charge becomes negative as the pH is increased, giving an increased OH^- to H^+ ratio on the colloid's surface. Finally, the authors suggested that Mn hydroxides are stable over a wide range of natural conditions and probably occur in natural waters whenever a sufficient source for Mn is present.

Loughnan (1969) stated that illite is by far the most abundant of the clay minerals in argillacous rocks. The author stated that K^+ is commonly leached from illite in shales to produce "mixed layered" soils such as are found in the eastern United States. The process of stripping K^+ from illites creates a soil "montmorillonite." A soil "chlorite" may be derived from this "montmorillonite" that has been stabilized with a d-spacing near 14A. Both the soil "montmorillonite" and "chlorite" are quite common in the eastern United States, according to the above author.

Loughnan (1969) also stated that complete degradation of illite to kaolinite may follow the reaction:

$$2KAl_2(AlSi_3)O_{10}(OH)_2 + 5H_2O \quad 3Al_2Si_2O_5(OH)_4 + 2KOH \ .$$

As both illite and kaolinite are found in the samples from the present study area, this process is possibly a mechanism for kaolinite production. The stream pH values of 6.0 in the Cumberland Plateau may be due, in some degree, to the presence of the basic KOH produced from this reaction. This topic lends itself to future studies.

Huang(1974) stated that halloysite and kaolinite may crystallize under the same conditions; however, any halloysite formed will tend to be spontaneously transformed to kaolinite due to ΔG_r° being negative. The rate of transformation is governed by other factors. Geologic occurrences of kaolinite and halloysite in ancient and modern environments are consistent with these predictions. The possible presence of halloysite is indicated in x-ray diffractograms from the current study.

CHAPTER III

RESEARCH METHODOLOGY

I. SAMPLING

Sediment samples were taken from stream beds by selecting areas of accumulation of sand sized and smaller material. Sediment was removed from these areas by means of random scooping of stream bed material. The sample stations were spaced approximately one-half mile apart with the locations marked on a topographic map, Figure 2.

In sampling, an effort was made to locate sites above and below major tributaries. Thus, determination of any effects that these tributaries have on the metal content of the sediment in the major stream was possible. Four samples (NR1-NR4) were taken from New River (one above and three below its confluence with Indian Fork), and five samples (IFA-IFE) were removed from the Indian Fork system (IFA was taken 0.1 mile upstream from the confluence with New River, while the other samples were taken at 0.5 mile intervals upstream).

A tributary, Joe Branch, which drains a portion of the basin north of IFB, flows from the vicinity of an abandoned deep mine. The tributary, Lick Branch, which joins Indian Fork upstream from IFC and IFD, originates primarily as drainage from an auger hole in a coal seam. This auger hole is shown in Figure 3.

Figure 4 is a photograph of the iron hydroxide-laden waters of Lick Branch entering Indian Fork. Notice the clear waters from Indian Fork in the top left portion of the picture.

R.F. Scale is 1":24,000".

IF = Indian Fork sampling sites.

NR = New River sampling sites.

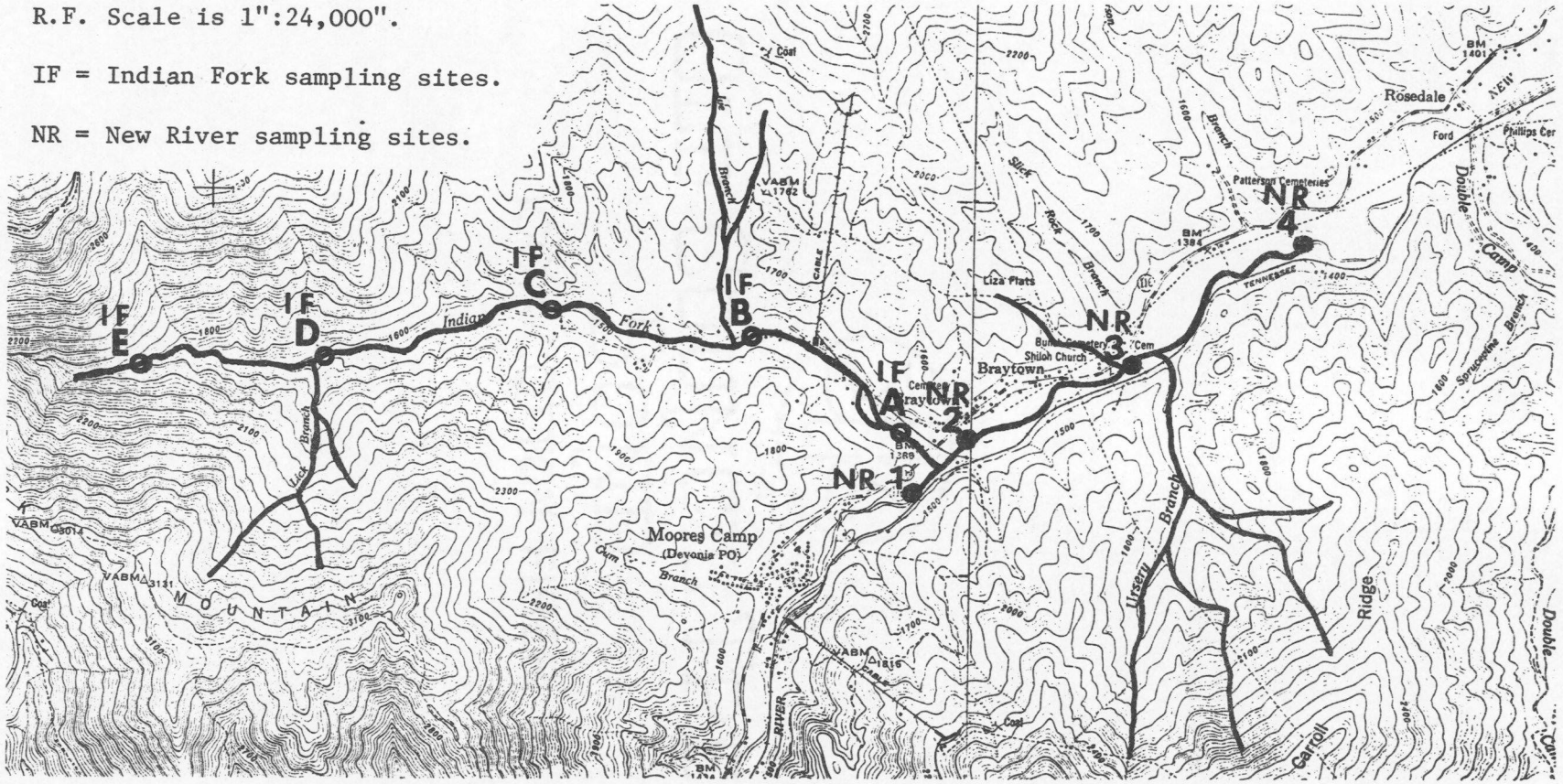


Figure 2. The portion of Fork Mountain Quadrangle which contains the area of sampling.



Figure 3. One of the sources of Lick Branch.



Figure 4. Confluence of Indian Fork and Lick Branch.

Figure 5 is typical of the Indian Fork streambed downstream from the Lick Branch influx. Boulders, gravel, and smaller-sized sediment are coated with crusts of hydrous Fe oxides.

The confluence of Indian Fork and New River is shown in Figure 6. The rust-colored waters in the left portion of the picture are from the runoff of Indian Fork. The muddy brown waters on the right side of the photograph illustrate the appearance of New River waters directly upstream from the Indian Fork entry.

II. METAL ANALYSIS

One pint (about 500 g dry weight) of grab sample as a suspension was taken at each sampling site and stored in a refrigerator at 2° to 4° C. Three separate analytical procedures were performed on each sample. The first two analyses were performed on separate portions of the <1 mm sample without dividing the <1 mm material into constituent size fractions. A third analytical procedure utilized size fractions of a portion of the original sample.

For the first two procedures the material to be analyzed was obtained from the original sample in the following manner: The original sample was well shaken and stirred and a randomly-selected aliquot of about 100 g (dry weight) was removed with a plastic spoon. This aliquot was wet sieved through a 1 mm (18 mesh) standard sieve. The >1 mm portion was air dried weighed and stored. After drying at 50°C, the <1 mm portion was weighed, carefully crushed to disaggregate, and thoroughly blended. Randomly selected portions of the <1 mm



Figure 5. Indian Fork streambed one mile downstream from Lick Branch.



Figure 6. Confluence of Indian Fork and New River.

material were removed for the first two analysis procedures.

In the first procedure, extractions (from 5.00 g of unground <1 mm material) of surface-adsorbed metals, and subsequent extraction of metals associated with hydrous oxides were accomplished. The surface-adsorbed metals were removed from the sediment by complexing with Na-citrate, a chelating agent. Hydrous Fe oxide affiliated metals were extracted by reduction with Na-dithionite. The reduced metal species were simultaneously chelated with Na-citrate. $NaHCO_3$ was used as a buffering agent to maintain a relatively constant pH during extractions. The Na-citrate and $NaHCO_3$ were used as a surface extractant mixture in order to determine what metals would be removed by this mixture in the reduction step; however, this mixture will not be used in the future because its high pH (8.3) creates an artifically alkaline environment for the normally acid samples.

The reducing agent, Na-dithionite, was chosen because it was not supposed to reduce MnO_2 or $Mn(OH)_2$; however, elevated Mn contents in the extract derived from this reduction reaction indicate that Mn may exist in a compound(s), in which the Mn ion occurs in more than one oxidation state. The metal content of this extract appears to be the sum of those metals affiliated with both Fe and some complex Fe-Mn hydrous oxides. Future work should be undertaken to determine exactly which metals are associated with the hydrous Fe oxides. The ability of hydrous Mn oxides to attract and transport trace metals is recognized. The effects of hydrous Mn oxide transport of trace contaminants in this (and other) fluvial systems could be quite important and should be more closely investigated in future studies.

In the second procedure, about 0.3g of the <1 mm sample (which had been ground so as to pass through a 200 mesh sieve) was dissolved in a mixture of perchloric and hydrofluoric acids. Both of the extracts and the solutions derived from acid digestion were analyzed for their metal contents by atomic absorption spectrophotometry. The calculations used are given in the appendix.

Finally, individual size ranges of the sediments were analyzed chemically. In order to do this the remaining original sample (about 400 g dry weight) was well stirred and mixed and a randomly-selected aliquot of about 200 g (dry weight) was removed with a plastic spoon. This aliquot was wet sieved to obtain >1 mm and <1 mm fractions. Size separations of <1 mm material were carried out by means of sedimentation, sieving, and centrifugation as described in the appendix. The resulting size ranges were: 0.2-2 μ (coarse clays); 2-5 μ (fine silts); 5-53 μ (coarse and medium silts); 53-105 μ (very fine sands); and 105-1000 μ (fine, medium, and coarse sands). These fractions were oven dried at 50°C, weighed, and stored. No material <0.2 μ was separated (or collected) due to the absence of this size of sediment.

About 0.3 g of each resulting size range (ground to pass through a 200 mesh sieve) was acid digested in the same manner as previously described. The resulting solutions were analyzed for metal content by atomic absorption spectrophotometry.

All >1 mm material was weighed and optically examined with a binocular microscope. The results of this optical examination are given in the appendix. This coarser material was not examined more

closely (or chemically analyzed) because it was mostly coal and bits of sandstones. It is presumed that this coarse fraction would have little affect on the sorption and transport of metal ions in the sediment of Indian Fork and New River.

III. X-RAY IDENTIFICATION

Preliminary identification of the minerals present in sediment from Indian Fork and New River was carried out by the use of x-ray diffraction. X-ray diffractograms were obtained from all size fractions of all samples. A number of minerals were present, and, as a result, not every peak was definitely assigned to one specific mineral.

The 105-1000μ, 53-105μ, and 5-53μ size ranges were examined using packed mounts. Only the 0.2-2μ and 2-5μ ranges were run on elutriated slides. The coarser size fractions were ground to a powder that would pass through a 200 mesh standard sieve. All samples were run at 2°2θ perminute and exposed to Cu K_α radiation at 17 kilowatts and 35 milliamps. The scale setting used was 1×10^2 and the time constant was two seconds.

After obtaining the initial diffractogram the 0.2-2μ and 2-5μ slides were heated to 550° for 90 minutes for the purpose of rudimentary clay mineral identification. The slides were not glycolated. After heat treating the slides were again x-rayed to detect any significant changes in d-spacings or peak heights. Results from this technique greatly facilitated the identification of the clay minerals.

IV. OBSERVATIONS ON THE REPRODUCIBILITY AND ACCURACY OF ANALYSIS

Several cross-checks for accuracy were carried out in the course of the present research. All analyses were conducted in duplicate. Each ensuing metal value presented in this thesis is an average of these duplicate analyses. Triplicate analyses of selected samples were also accomplished with the results presented in the appendix, Tables XIV and XV. The deviation of these analyses was generally less than 10%.

Intralab comparisons on six unidentified samples were performed by Gregory Upham, who is engaged in similar research on an unstripped drainage basin, and the author. The results of these comparison analyses are presented in Table XVI in the appendix.

In the course of analyses the author observed a discrepancy in metal values for Cr. It was found that there was a chemical interference of Cr due to the nature of the sample matrix. The effect of the problem was that standard solutions reacted proportionally greater to variations in flame intensity than did the samples. The absorption of Cr in the samples appeared to be too high under lean flame conditions and rich flame conditions gave Fe interference.

Dr. J. H. Rule, Department of Geological Sciences, University of Tennessee at Knoxville, studied the factors contributing to interference in the samples. He concluded that the presence of Fe and varying amounts of perchloric acid as portions of sample matrix were the main sources of the interference. It was found that 2% NH_4Cl, 2% $HClO_4$, 1000µg/g Fe, and 0.006 M EDTA when added to the standards

caused their response to flame intensities to be proportional to the response of the samples. The presence of 2% NH_4Cl allowed uniform Cr absorption in varying concentrations of Fe from 400 µg/ml to 1200 µg/g. (Varying amounts of Fe were inherent among all samples. By digesting all samples to complete dryness the effect of perchloric acid salts on all samples would have been uniform.) The samples were then spiked with a Cr releasing agent to overcome the interference. The releasing agent was added so that the samples were 2% NH_4Cl and 0.006 EDTA. Apparently satisfactory results were obtained utilizing this method.

A check for contaminants, possibly added during sample preparation, was performed. Four identical aliquots of one sample were ground in a sintered Al_2O_3 (Diamondite) mortar. Varying amounts of scraping with a stainless steel spatula were employed in removal of the aliquots. Nickel concentrations increased nearly 10% in the excessively scraped aliquots, while no other metals varied over 5% from one aliquot to another.

CHAPTER IV

RESULTS AND DISCUSSION OF ANALYSES OF LESS THAN ONE MILLIMETER SAMPLES

Table I presents the average metal concentrations of all <1 mm samples from Indian Fork and New River. It is obvious from the data in this table that iron is by far the most abundant metal detected. Manganese concentrations are about two orders of magnitude fewer than those of Fe; however, Mn is approximately one to two orders of magnitude more abundant than each of the other metals present in the samples.

There is a marked increase in the concentrations of Fe and Mn at sampling sites downstream from the influx of tributaries. Perhaps due to their higher general abundance (together with the fact that hydroxides of these cations can transport other metal species), Mn and Fe are the best indicators of tributary influence. Arrows in Table I indicate the approximate locations of the tributaries previously mentioned: Lick Branch, Joe Branch, and Indian Fork.

It is evident from examination of Table I that Joe Branch affects the metal concentrations in the Indian Fork sediment more than does Lick Branch. The metal levels are much higher directly downstream from the confluence with Joe Branch than they are downstream from Lick Branch's entry into Indian Fork. As previously stated, Joe Branch drains from the vicinity of a deep mine.

Table I

Metal Concentrations for <1 mm Samples
(in μg/g) from Acid Dissolutions

Location	Cr	Cd	Co	Cu	Ni	Pb	Zn	Mn	Fe
IFE	55	3	33	19	43	41	169	733	36,220
→	Entry of Lick Branch								
IFD	44	3	26	20	33	90	168	682	47,620
IFC	78	3	39	29	41	107	189	897	63,376
→	Entry of Joe Branch								
IFB	87	4	39	33	49	130	229	1110	92,339
IFA	55	3	32	25	42	82	147	705	45,629
Averages	64	3.2	34	25	42	90	180	825	57,037
↓ Downstream									
NR1	66	3	35	25	43	82	194	507	38,731
→	Entry of Indian Fork								
NR2	87	5	51	31	66	162	715	566	71,551
NR3	57	4	31	30	42	82	239	700	43,246
NR4	77	3	36	28	43	54	207	650	42,205
Averages	72	3.8	38	29	49	95	339	606	48,933

The influx of Indian Fork has a much greater effect on the New River sediment than does either of the tributaries (which enter Indian Fork) on the sediment in Indian Fork. Table I, page 23, presents data which shows that all levels of metals are noticeably higher at NR2, which is directly downstream from Indian Fork's entry, than are the corresponding metal values at NR1, which lies upstream from the confluence. This elevated metal content is not unexpected since Indian Fork adds a noticeable sediment load to the existing sediment already being carried by New River. Diminishing metal concentrations downstream from NR2 can be attributed to the dilution effect from New River and its tributaries, such as Ursery Branch, Figure 2, page 13, on the material added by Indian Fork.

The average metal concentrations for each stream in Table I, page 23, suggest that the content of metal in both streams is very nearly the same. Zinc, Fe, and Mn are the only metals which vary between the two streams by more than 10%. Apparently Zn is less concentrated in the Indian Fork drainage basin than it is in proximal basins. Conversely, Fe and Mn seem to be more concentrated in the Indian Fork system than in the New River system.

Figure 7 is a graphical presentation of metal concentrations, excluding Mn and Fe, at each sampling site in Indian Fork. Iron and Mn are deleted on all graphs of total metals because of their extremely high concentrations which would make it difficult to discern variations in the total concentrations of the less abundant metals. The general trend shown by Figure 7 is enrichment of metals at localities

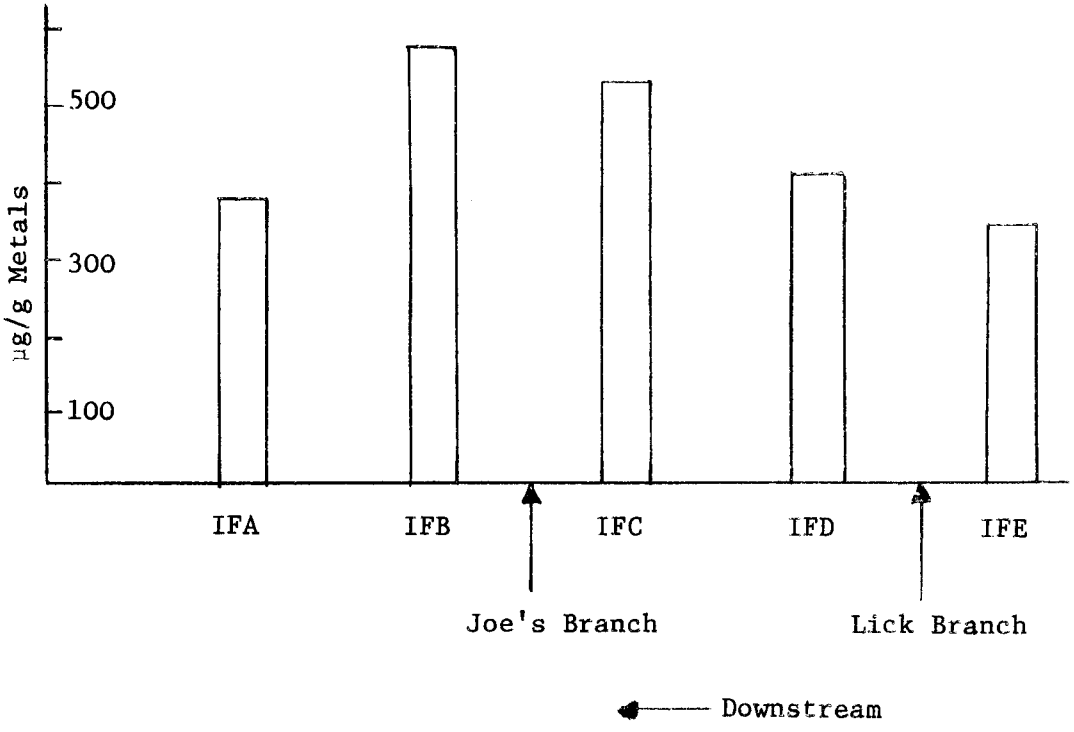


Figure 7. Sum of metal concentrations at the localities along Indian Fork (excluding Fe and Mn) from acid dissolutions.

downstream from tributaries. A gradual increase is noticeable downstream from IFE. This increase is attributed to the settling of small suspended particles that were contributed by Lick Branch.

This settling phenomena is not observed downstream from Joe Branch because it is an intermittent stream and carries a less sedimentalogically mature load than does Lick Branch. The sediments contributed by Lick Branch are of a finer grain size than those contributed by Joe Branch. Data to support this conclusion will be presented in another portion of this paper.

Most of the metals studied from Indian Fork sediment follow the same general trend as shown in Figure 7, page 25; however, Cd, Co, and Ni do not show the concentrating effects of tributaries as much as the other metals. Cadmium, in fact, shows very little deviation in concentrations among sample sites. This fact may indicate that strip mining in this basin has had very little effect on the Cd content in the streambed sediment.

The concentrations of three selected metals (Pb, Ni, and Zn) from Indian Fork are shown in Figure 8. Lead and Zn vary noticeably among the sampling sites, while Ni shows much less variation. Lead and Zn levels in the Indian Fork sediment are at least twice the metals' average crustal abundance in shales. These average crustal abundances in shales for Pb and Zn are 20 ppm and 80 ppm, respectively (Krauskopf, 1967). The processes involved in localizing these metals in Indian Fork sediment seem to be quite effective. Of course, the levels of accumulation of these metals, as well as all others studied,

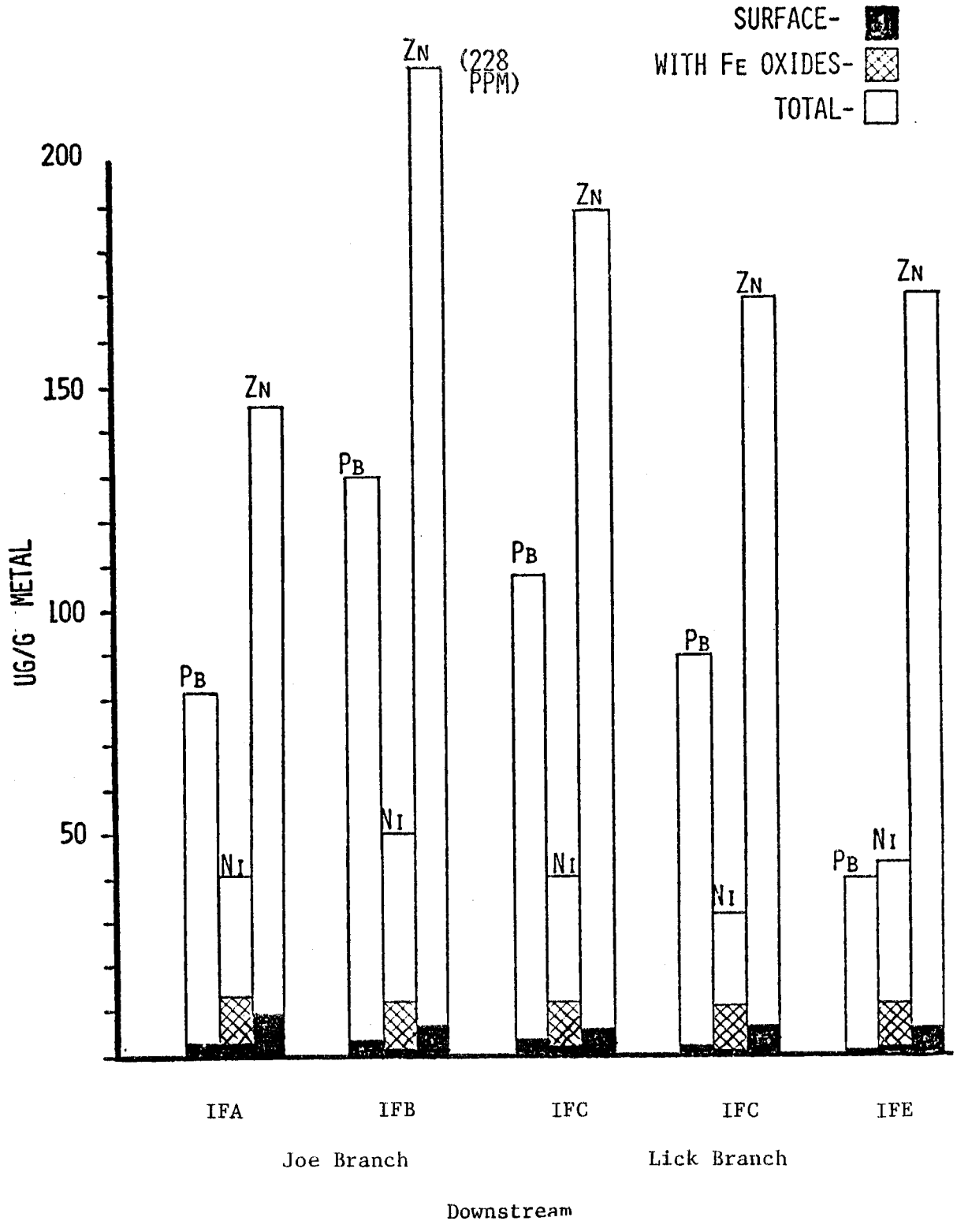


Figure 8. Selected metals from streambed sediment from Indian Fork Basin.

are due not only to concentrating agents (such as cation adsorption by clay minerals) in the fluvial system but also to the original concentrations of each metal in the surrounding source material.

Figure 9 represents the metal accumulations in the sediment from New River sampling localities (excluding Fe and Mn). Immediately downstream from the Indian Fork confluence a significant rise in metal content occurs. The question arises as to whether this increase is due to enrichment of the entire sediment sample with metals or if it is due to greater accumulations of certain sediment sizes which have greater metal concentrations. This subject will be considered in the next chapter.

As in the case of the metals from Indian Fork localities, most of the metal concentrations in New River sediments rise at the site most heavily affected by tributary (Indian Fork) influence. An exception to this trend in the New River sediment is Mn. Although an increase in most other metals is noted at NR2, the point of highest Mn content is NR3. There are several plausible explanations for this distribution. The Mn could be transported in the form of a hydrated colloid which begins to accumulate on New River sediment downstream from its injection into the system from Indian Fork. A Mn colloid may also be flocculating to produce aggregates of hydroxide particles which settle near this site. The problem with suggesting a colloidal mechanism for Mn in this case is that there is no simultaneous rise in trace metals with the increased Mn. If Mn colloids are good agents for the transport of cations, then a rise in these cations should occur where Mn concentrations are elevated. Some source other than Indian

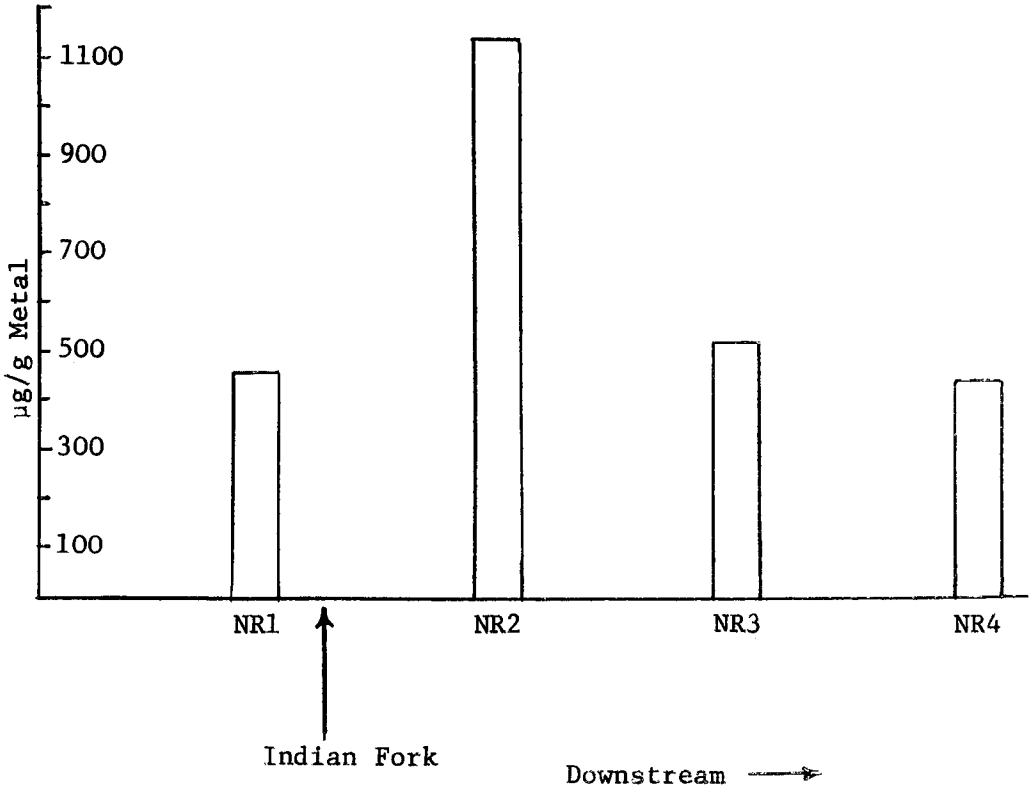


Figure 9. Sum of metal concentrations at the localities along New River (excluding Fe and Mn) from acid dissolutions.

Fork could be the cause of elevated Mn levels at NR3. This source could be the unnamed tributary directly south of NR3. If this small stream is carrying elevated amounts of Mn, due perhaps to the influence of one of several dwellings in the area, it could be the source of higher Mn levels at NR3. Future studies should deal with the question of this apparently anomalously high Mn concentration without concomitant trace metal accumulations.

The concentrations of three selected metals at the New River sampling sites are shown in Figure 10. The influence of Indian Fork is quite interesting. Briefly, Ni is least affected by the tributary (Indian Fork) influx of the three metals; Pb is noticeably (twofold) increased by the influx of Indian Fork; Zn is dramatically (threefold) enriched in the sediments at NR2. The enrichment appears to be directly related to the Indian Fork entry. All three metals show decreasing concentrations downstream from Indian Fork due to dilution by New River material.

The relationships of metals to surface adsorption on sediment and the affiliation of metals with hydrous oxides are useful in understanding the modes of occurrence of these cations in the sediment. Table II illustrates these relationships. The samples had less than 10% of the total amount of each metal associated with surface adsorption. Most of each metal was found to be associated with the hydrous oxides. MnO_2 and $Mn(OH)_2$ were not supposed to be affected by the reducing agent ($Na_2S_2O_4$); however, reduction of other forms of Mn hydrous oxides may account for the high Mn values in this category. Also, a hydrous oxide with both Mn and Fe in cation sites could be

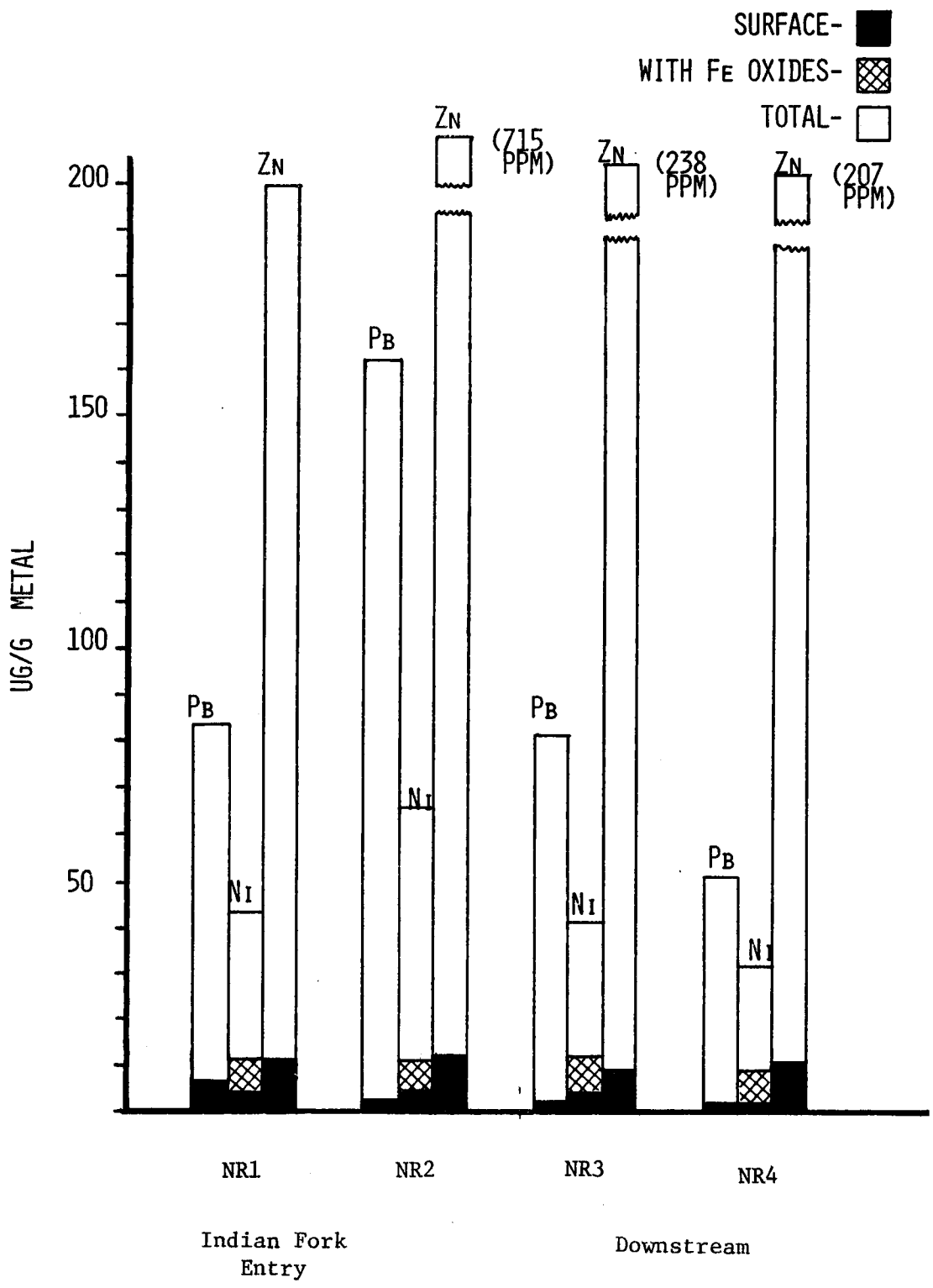


Figure 10. Selected metals from New River streambed sediment from acid dissolutions.

Table II

Comparison of Metal Concentrations from Chemical Extracts: Surface Adsorption (S Column) and Adsorption on Hydrous Oxides (H Column) in µg/g

Location	Cr		Cd		Co		Cu		Ni		Pb		Zn		Mn		Fe	
	S	H	S	H	S	H	S	H	S	H	S	H	S	H	S	H	S	H
IFE	*	8.6	0.1	1.8	1.4	11.4	0.8	2.9	1.4	9.9	0.8	*	6	#	15	550	172	20,900
IFD	*	8.6	0.1	1.8	1.3	13.4	0.8	4.0	1.1	9.9	2	*	6	#	10	550	260	26,400
IFC	*	9.5	0.12	1.5	1.8	14.3	0.8	4.0	1.7	11	2.4	*	4.8	#	16	660	292	34,100
IFB	*	14.3	0.16	2.6	1.4	14.3	0.9	4.4	1.4	13.2	2.8	*	6	#	10	726	232	46,862
IFA	*	7.7	0.14	1.8	1.7	11.	0.8	2.9	2.	11	2	*	8.8	#	15	550	240	27,500
NR1	*	7.7	0.14	1.5	2.4	7.2	1.4	2.9	1.9	7.5	3.2	*	8.0	#	8	220	520	23,100
NR2	*	9.5	0.24	2.2	1.6	8.4	1.6	4.0	2.4	8.4	1.2	*	12.5	#	17	264	580	39,600
NR3	*	8.6	0.22	1.8	2.8	7.9	1.4	2.9	3.2	7.9	2	*	8.8	#	20	264	420	30,360
NR4	*	7.7	0.26	1.8	2.3	7.1	1.4	2.9	2.1	7.5	2	*	12.5	#	13	242	440	23,100

* Below Limits of Detection.

Indeterminable Due to Reagent Contamination.

the main form in which Mn occurs. Further studies in this area should be able to delineate the mode of Mn occurrence.

Cadmium illustrates a good example of the general trend stated above. Four percent of the total Cd is present in the surface adsorbed group; 63% of the total Cd is present in the hydrous oxide affiliated group; the remaining 33% of total Cd must be present in either the form of an unreduced compound, cations sorbed to the sediment, or a cation in lattice positions in a mineral. The presence of this 33% of total Cd as sorbed cations on the sediment is least likely.

Most of the Fe (about 75% of the total Fe) exists in the hydrous oxide form. The hydrous Fe oxide is a very important means of transportation of other metals, as previously stated. It is possible to infer that the elevated trace metal levels in the hydrous oxide affiliate category are all due to the reduction of hydrous Fe oxides. Percentages of the total metals associated with the hydrous Fe oxides (generally about 40%) are found in Table XVII in the appendix. It is also possible to infer that Mn oxides play an important role in metal transport. Again, this area bears further investigation.

A noteable exception to the general trend of associations is Pb. It occurs below the limit of detection in hydrous oxide affiliation, and only a small amount is found in the adsorbed category. This knowledge, along with the fact that the Pb content in the sediment increases with decreasing grain size, points to the conclusion that the Pb present is in a strongly bonded state. It may exist as a distinct Pb compound or as a substitutional cation in illite for

K^+ . Extremely elevated $SO_4^=$ contents in Indian Fork waters, reported by Minear, Department of Environmental Engineering, University of Tennessee at Knoxville (1975, personal communication) to be on the order of 700 ppm and above, and an x-ray diffraction peak from Indian Fork sediments corresponding to the strongest peak of $PbSO_4$, both suggest that Pb may occur in these sediments as anglesite. Further size and density separations should be employed for a more detailed evaluation of this data.

The associations of Cr are also worthy of note. Chromium is present in noticeable amounts (about 16%) associated with the hydrous oxides, but it occurs below detection limits in the surface adsorbed category. Chromium may exist in crystalline lattice sites or as a hydrous oxide affiliate. It may also be present in a form so strongly adsorbed as not to be removed by Na-Citrate.

CHAPTER V

RESULTS AND DISCUSSION OF SIZE FRACTION ANALYSES

I. RESULTS OF SIZE SEPARATION

After separation of each sediment sample into the various size fractions, these fractions were weighed and stored. The weight percentages of all size fractions from each sampling site are presented in Table III. Generally, the New River samples have the major portion of their sediment in the 5-53μ size range, while the majority of Indian Fork sediment is present in the 105-1000μ fraction. Also note that a greater percentage of New River sediment rather than Indian Fork sediment falls into the 2-5μ and 0.2-2μ size ranges. This increase in smaller sizes of sediment is a result of lower stream velocities in New River than in Indian Fork.

II. RESULTS OF INDIAN FORK SIZE FRACTION ANALYSES

An examination of the metal concentrations in the several size fractions of the samples reveals some trends and relationships which are not evident in the data presented in the previous chapter. The average metal concentrations of the several Indian Fork size fractions are given in Table IV. The outstanding relationship that these data suggest is that all nine metals are concentrated in the finer grain sizes. There is a very abrupt increase in metal concentrations of the 2-5μ size range over the metal levels in the coarser fractions.

Table III

Percentage of Sediment Sizes from Sampling Localities

	Location	>1mm	105-1000μ	53-105μ	5-53μ	2-5μ	0.2-2μ	Totals
	IFE	14	70	6.5	6.5	1.6	1.4	100
	IFD	19	69	2.3	5.8	3.1	1.1	100.3
	IFC	10	59	14	14	1.7	1.6	99.7
	IFB	13	65	6	12	2.4	1.2	99.6
	IFA	18	47	15	17	1.7	1.4	100.1
↓ Downstream	- - - - - -							
	NR1	8.1	21	14	46	6.6	5.3	101
	NR2	.2	6.4	5.7	51	28	9.4	100.7
	NR3	2.5	53	11	27	5.8	.6	99.6
	NR4	1.3	14	14	59	7.2	4.8	100.3

The fact that percentages do not equal 100 is due to rounding off of numbers following scientific conventions.

Table IV

Average Metal Concentrations of Indian Fork Sediment of Each Size Fraction (in μg/g)

	Cr	Cd	Co	Cu	Ni	Pb	Zn	Mn	Fe
IFA:									
105-1000μ	53	2.9	27	18	50	33	82	1148	37,825
53-105μ	68	1.8	20	16	37	35	60	561	39,234
5-53μ	46	3.9	31	13	41	33	92	464	37,072
2-5μ	106	5.2	73	38	104	60	198	1650	117,633
0.2-2μ	106	4.7	106	52	111	83	241	1467	82,534
IFB:									
105-1000μ	69	4.0	27	26	72	49	141	1397	82,526
53-105μ	59	2.0	25	21	49	37	70	750	38,351
5-53μ	53	3.2	39	14	52	33	82	713	40,448
2-5μ	106	5.8	85	42	109	61	203	2095	74,752
0.2-2μ	143	4.9	83	58	117	83	256	1687	90,097
IFC:									
105-1000μ	53	3.2	29	22	54	36	85	1170	47,128
53-105μ	42	1.8	22	22	42	37	67	549	39,312
5-53μ	57	2.7	36	14	49	33	119	949	48,208
2-5μ	123	6.4	97	51	109	63	218	2302	100,672
0.2-2μ	144	6.5	46	60	108	72	203	1600	104,519
IFD:									
105-1000μ	46	3.2	26	17	52	36	83	946	49,023
53-105μ	51	2.6	20	16	47	37	66	474	43,137
5-53μ	75	3.9	45	15	50	43	117	750	58,859
2-5μ	119	4.7	128	36	110	62	167	1836	71,167
0.2-2μ	119	4.6	70	46	99	87	204	1502	94,559
IFE:									
105-1000μ	63	3.5	26	22	50	43	95	974	40,359
53-105μ	36	2.4	22	13	39	37	66	515	35,468
5-53μ	57	2.7	34	16	58	35	110	703	42,117
2-5μ	88	6.2	103	39	109	49	173	2174	40,782
0.2-2μ	115	4.8	64	76	102	80	216	2269	64,851

The 0.2-2μ size range has the same high level of concentrations as does the 2-5μ fraction. Also, the 105-1000μ range has some higher metal concentrations than does the next finer size fractions. These elevated levels in the largest size fraction may be attributed to the encrustation of hydrous oxides on these larger particles. This topic bears further investigation.

A comparison of data from Table V with Table IV, page 37, illustrates the effects of the Indian Fork basin in concentrating metals in certain size fractions of sediment. Generally, the concentration of metals in the three coarsest size fractions correlate approximately with the corresponding metals' average concentrations in shales. The two finer-grained fractions exhibit metal concentrations much greater than the average levels in shales. Some of the metals, Cd and Pb for example, occur well above their average in shales even in the coarsest size fraction. Again, it is possible that elevated metal values in the 105-1000μ range of particles may be due to hydrous oxide encrustation.

Nickel is worthy of note because it occurs in concentrations lower than its shale abundance in the coarser sediment fractions, and about equal to shale values in the finer-grained sediment. It may be concluded from these facts, that no matter how effective the enrichment of Ni by strip mining, the source strata are too poor in Ni initially to allow high levels of accumulations of this metal in the sediment; or, perhaps Ni is being preferentially removed from the system. Copper follows the same concentration relationships as does

Table V

Average Elemental Abundance in μg/g

	Cr	Cd	Co	Cu	Ni	Pb	Zn	Mn	Fe
Entire Crust	100	0.2	25	55	75	12.5	70	950	5.6×10^4
Shales	100	0.3	20	57	95	20	80	850	4.7×10^4

Ni, and the same low initial (local) abundance is inferred. The remaining metals tend to occur in concentrations near their average shale abundances in the coarser size fractions. They become more concentrated in the 0.2-2μ and 2-5μ size ranges.

In Table IV, page 37, it can be seen that the influx of tributaries does not affect metals in all of the size fractions to the same degree. Generally, the smaller-sized particles are more affected by the proximity of a tributary than are the larger grain sizes. A partial explanation for this occurrence may be that these tributaries are draining areas heavily laden with trace metals due to mining. These trace metals may become adsorbed to the finer sediment (clays) and, thus, the finer-grained material will show an increase in metal concentration due to the tributary influence.

Figure 11 displays the trend of increased metal concentrations in the finer-grained sediment. The data for this figure was compiled from the total of all metal averages from each size fraction, excluding Mn and Fe. The 2-5μ and 0.2-2μ size fractions are about 50% more concentrated in metals than any of the other size fractions.

The percent of each metal found in the constituent size fractions of Indian Fork sediment is presented in Table VI. Examining this data, it is evident that Zn follows the general trend of greater concentration in the finer grain sizes. Zinc is also greatly influenced by tributary influx. Zinc values increase in the 0.2-2μ and 2-5μ size fractions; and Zn in Table I, page 23, is seen to be influenced by tributary proximity (with higher values at IFB and

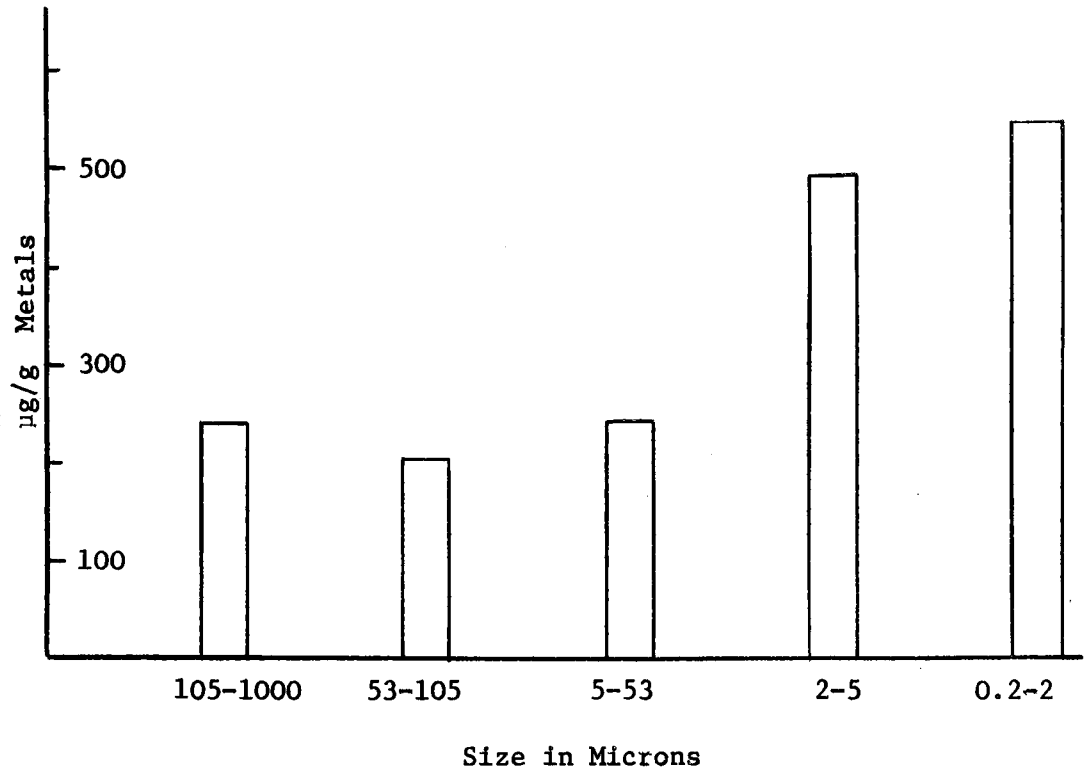


Figure 11. Sum of the average metal concentrations in each size fraction of Indian Fork sediment (excluding Fe and Mn).

Table VI

Percentage of Metals in Indian Fork Size Fractions

Size, μ	Cr	Cd	Co	Cu	Ni	Pb	Zn	Mn	Fe
105-1000μ	14	17	11	14	15	16	14	18	17
53-105μ	13	11	9	12	12	15	10	9	13
5-53μ	14	17	14	9	14	14	15	12	15
2-5μ	27	29	38	27	30	24	28	33	27
0.2-2μ	32	26	29	38	30	32	33	28	29

IFC). Thus, combining data from size fraction analyses and the analyses of <1 mm sample it is possible to suggest that Zn will be found in its highest concentrations (in this system) in the finer sizes of sediment downstream from mine affected tributaries. In fact, we may be able to predict these relationships for most of the metals studied.

Copper displays a tendency to be concentrated in the finer sizes of sediment, but it shows a definite preference for the 0.2-2μ fraction, since it is readily adsorbed by clay particles. In fact, Cu is more concentrated (percentage wise, 38%) in this size range than any other metal studied. This elevation of Cu values in the finest grain sizes can be explained by its affinity for clay-sized materials throughout the sedimentary regime. Due to possible low initial concentrations in the source strata (as previously discussed), Cu values in the 0.2-2μ fraction do not exceed the average abundance of this metal in shales.

Table VII presents the sites where the highest concentration of each metal in each size fractions of Indian Fork sediment occurred. An interesting phenomena that these data illustrate is the grouping of maxima according to certain localities. The finer-grained sediments generally have concentration maxima at the sites affected by Lick Branch, while the sites affected by Joe Branch are displaced toward the larger particles. This segregation of maxima may reflect the characteristics of the major quantity of sediment from each tributary. The larger, continuously-flowing, stream -- Lick Branch --

Table VII

Site of the Highest Concentration of Each Metal
Per Size Fraction from Indian Fork Sediment

Metal	105-1000μ	53-105μ	5-53μ	2.5μ	0.2-2μ
Cr	IFB	IFA	IFD	IFC	IFC
Cd	IFB	IFD	IFC, IFA	IFC	IFC
Co	IFC	IFB	IFD	IFD	IFA
Cu	IFB	IFB, IFC	IFE	IFC	IFE
Ni	IFB	IFB	IFE	All Sites	IFB
Pb	IFB	IFB, IFC IFD, IFE	IFD	IFA, IFB IFC, IFD	IFD
Zn	IFB	IFB	IFC	IFC	IFB
Mn	IFB	IFB	IFC	IFC	IFE
Fe	IFB	IFD	IFD	IFA	IFC

- = Sites Affected by Lick Branch.

= = Sites Affected by Joe Branch.

may carry more finer-grained sediment than the intermittent Joe Branch. The larger particles brought into Indian Fork by Joe Branch may settle out almost immediately, precluding much affect on sediment farther downstream than IFB. The finer-grained sediment added to Indian Fork by Lick Branch appears to finally settle near IFC, according to Table VII.

The data (thus far presented on analyses of size fractions of Indian Fork sediment) have shown marked increases in metal concentrations in certain size fractions. In fact, the metal concentrations in some of these size fractions are higher than corresponding metal values obtained from the analyses of the <1 mm samples. The actual contribution of each fraction to the metal content of one gram of total sediment is proportional to the weight percent of that size fraction in the sediment. Table VIII presents the actual amounts of trace metals found in one gram of (collected) sediment (per size fraction) from each Indian Fork sampling site. These data represent the contribution, of each size fraction analyzed, to the total trace metal content of the stream sediment collected for this study. This method of data presentation was chosen in order to predict, as closely as possible, the actual amounts of trace metals that each size fraction donates to one gram of the approximately sand-sized and smaller sediment in the stream. Another reason this mode of data presentation was utilized deals with the different characteristics of sediment between the two streams. When the >1 mm material is included, it is possible to discern the greater percentage of these larger sediment sizes in the Indian Fork system. Another

Table VIII

Metal Contribution from Each Size Fraction of Indian Fork Sediment (in μg/g)

	Cr	Cd	Co	Cu	Ni	Pb	Zn	Mn	Fe
IFA:									
105-1000μ	25	1.4	13	8.5	24	16	39	540	17,778
53-105μ	10	0.27	3	2.4	5.6	5.0	12	84	5885
5-53μ	7.8	0.66	5.3	2.2	7.0	5.6	16	79	6302
2-5μ	1.8	0.09	1.2	0.7	1.8	1.0	3.4	28	2000
0.2-2 μ	1.5	0.07	1.5	0.73	1.6	1.2	3.4	21	1156
IFB:									
105-1000μ	45	2.6	18	17	47	32	92	908	53,642
53-105μ	3.5	0.12	1.5	1.3	2.9	2.2	4.2	45	2301
5-53μ	6.4	0.38	4.7	1.7	6.2	4.0	9.8	86	4854
2-5μ	2.5	0.14	2.0	1.0	2.6	1.5	4.9	50	1794
0.2-2μ	1.7	0.06	1.0	0.7	1.4	1.0	3.1	20	1081
IFC:									
105-1000μ	31	1.9	17	13	32	21	50	690	27,806
53-105μ	5.9	0.25	3.1	3.1	5.9	5.2	9.4	77	5504
5-53μ	8.9	0.41	5.4	2.1	7.4	5.0	18	142	7231
2-5μ	2.1	0.11	1.7	0.87	1.9	1.1	3.7	39	1711
0.2-2μ	0.9	0.10	0.74	0.96	0.70	0.20	3.3	26	1672
IFD:									
105-1000μ	32	2.2	18	12	36	25	57	653	33,826
53-105μ	1.2	0.06	0.46	0.37	1.1	0.85	1.5	10.9	992
5-53μ	4.4	0.23	2.6	0.87	2.9	2.5	6.8	44	3414
2-5μ	3.7	0.15	4.0	1.1	3.4	1.9	5.2	57	2206
0.2-2μ	23	0.05	0.77	0.51	1.1	0.96	2.2	17	1040
IFE:									
105-1000μ	44	2.5	18.2	15.4	35	30	67	682	28,251
53-105μ	2.3	0.16	1.4	0.85	2.5	2.4	4.3	34	2305
5-53μ	3.7	0.18	2.2	1.04	3.8	2.3	7.2	46	2738
2-5μ	1.4	0.1	1.7	0.62	1.7	0.78	2.8	35	653
0.2-2μ	2.1	0.07	0.9	1.06	1.43	1.12	3.02	32	908

mode of data presentation is to leave out the >1 mm material in compilation of these data. This omission of material in calculation causes the metal contributions of each size fraction to appear greater, Table XXV in the appendix; however, the metal contents of the sediment, of course, do not vary. The only difference between these two methods of data compilation is that the former method presents metal contributions on a basis of contribution to 100% of sediment collected while the latter is based on size fraction contributions to 100% of sediment analyzed. Since the >1 mm portion of sediment was not analyzed, it was not included in the latter form of data compilation. The high flow regime of the Indian Fork channel allows major accumulation of only the larger sediment sizes; the smaller-sized fractions are swept out of the systems into New River. Thus, the major contribution to the total metal in one gram of sediment comes from the coarser material in the Indian Fork samples.

III. RESULTS OF NEW RIVER SIZE FRACTION ANALYSES

The tendency for the greatest concentration of metals to be in the finer-grained material is seen most explicitly in the New River sediments. As the data in Table IX exhibits, the concentrations of all metals (except Mn) increase in the 2-5μ and 0.2-2μ ranges. Comparison of data between Table IX and Table IV, page 37, points out that the sediment in New River generally contain about 10% more of any given metal in corresponding size ranges than does Indian Fork. That this trend is reversed in several cases may reflect the similar

Table IX

Average Metal Concentrations of New River Sediment of Each Size Fraction (in μg/g)

	Cr	Cd	Co	Cu	Ni	Pb	Zn	Mn	Fe
NR1:									
105-1000μ	59	3.2	23	31	46	28	99	1393	41,721
53-105μ	65	2.5	29	29	47	27	93	391	30,435
5-53μ	67	2.6	49	23	48	27	101	510	30,409
2-5μ	108	4.2	79	41	98	48	204	794	53,042
0.2-2μ	112	6.2	98	53	133	51	271	1191	102,670
NR2:									
105-1000μ	47	3.3	27	29	48	27	86	1356	38,467
53-105μ	49	3.3	28	30	48	28	102	364	32,789
5-53μ	80	4.2	48	26	64	28	124	453	41,508
2-5μ	110	4.3	79	30	91	45	180	812	69,548
0.2-2μ	114	7.1	104	54	117	51	226	1813	102,661
NR3:									
105-1000μ	46	2.8	20	34	41	27	80	1568	38,068
53-105μ	61	4.7	32	32	66	27	123	547	29,591
5-53μ	65	3.6	52	23	65	27	133	787	38,088
2-5μ	106	5.8	90	55	127	51	294	1962	94,588
0.2-2μ	126	6.5	99	71	156	50	319	1819	104,787
NR4:									
105-1000μ	46	3.5	25	36	53	27	87	1655	33,499
53-105μ	68	3.8	35	30	52	28	119	615	29,876
5-53μ	66	3.4	53	23	57	27	104	640	30,295
2-5μ	108	6.0	80	41	114	44	228	1585	51,012
0.2-2μ	123	5.4	104	56	123	50	228	1820	95,168

strata which the two basins drain. This similarity of source rock does not allow either stream to become drastically enriched in a particular metal. It is logical to assume that the strip mining around the New River basin would liberate trace metals in the same magnitude of concentration as would the strip mining around Indian Fork.

Figure 12 graphically presents the now familiar trend for metals to be concentrated in the 0.2-2μ and 2-5μ sizes. Clearly, these fractions contain the highest levels of metal accumulation. The distribution of metals in New River size fractions shown in Figure 12 corresponds very closely with the distribution shown for Indian Fork in Figure 11, page 41. Again, in New River the two finest size fractions are at least 50% higher than any of the coarser-grained fractions.

The data in Table X presents the size affinities for individual metals from New River sediments. Both Co and Cd, which were most concentrated in the 2-5μ range in Indian Fork, Table VI, page 42, now exhibit highest accumulations in the 0.2-2μ material. Again, Cu shows a tendency to be highly concentrated in the finest-grained sediment. Iron is heavily concentrated in the 0.2-2μ size. Elevated Fe levels can be explained, perhaps, by flocculation and accumulation of hydrous oxides about suspended particles in the New River. These flocculants would then settle and the sediment content of the finer-grained fractions would increase. Of course, the lower stream velocities of New River could allow settling of this sized material which would be in suspension in Indian Fork waters. A large percentage (27%) of the Mn in New River sediments is present in the 105-1000μ

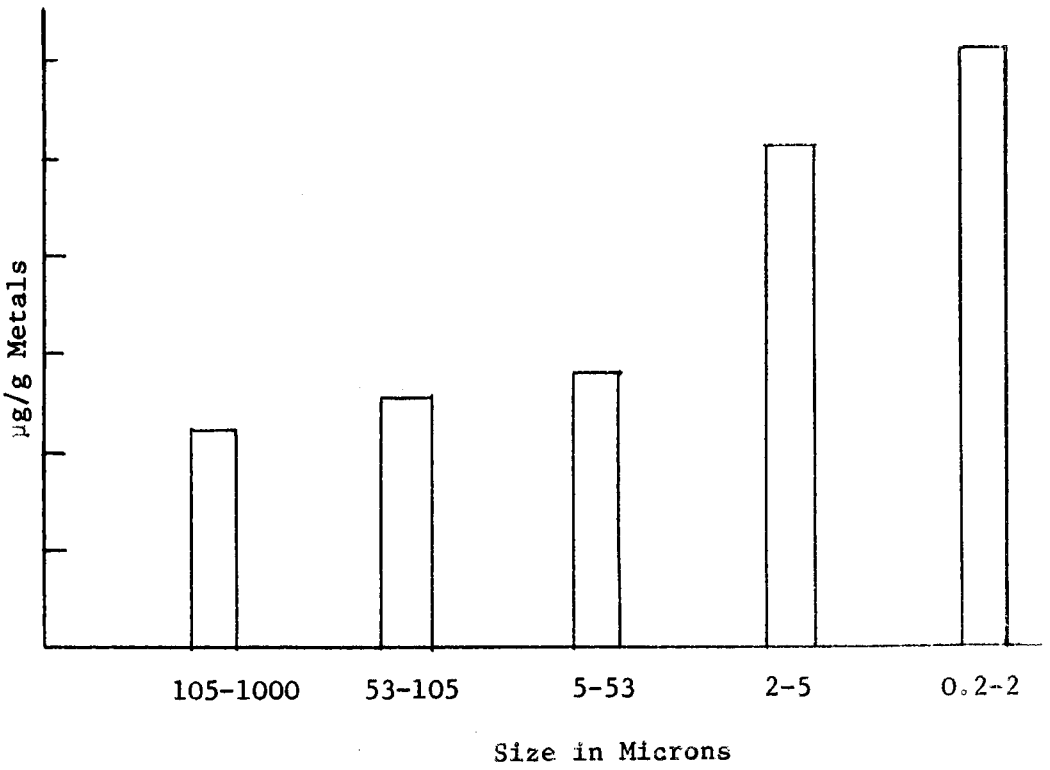


Figure 12. Sum of the average metal concentrations in each size fraction of New River sediment (excluding Fe and Mn).

Table X

Percentage of Metals in New River Size Fractions

Size, μ	Cr	Cd	Co	Cu	Ni	Pb	Zn	Mn	Fe
105-1000μ	12	15	8	17	12	15	11	27	14
53-105μ	15	17	11	16	13	15	14	9	11
5-53μ	17	16	18	13	15	15	14	11	13
2-5μ	27	24	28	22	27	26	28	23	25
0.2-2μ	29	29	35	31	33	28	33	30	37

size range. Although there is no corresponding trace metal increase in this fraction, the high Mn accumulation could be due to encrustation of hydrous oxides on these larger grains. Since no Mn minerals were identified in the sediment, the apparent anomalously high Mn content of the 105-1000μ fraction is an unresolved phenomena. Future work definitely should be centered about the role of Fe and Mn hydrous oxides in trace metal transport in these fluvial systems.

Table XI presents the sites of highest concentrations of each metal in each size fraction of New River sediment. The data suggests that the same process of settling is discernible here as it was in Indian Fork data. The settling is more subtly shown in the New River data. Most of the highest metal concentrations occur at NR3. Of these maxima occurring at NR3, most are associated with the smaller sizes of material. In fact, each maximum in the 0.2-2μ and 2-5μ fractions (except two) occurs at NR3. The fact that elevated metal levels occur at NR3 in the coarser-grained material could be due to the influence of the unnamed tributary just upstream from this sampling site, Figure 2, page 13. Since the New River tributary system interacts with the sediments added by Indian Fork, it is impossible to be certain of the process of enrichment (due to downstream settling) in the New River sediments.

In Table XII the actual contribution from each size fraction (per gram) of New River sediment is presented. Comparing Table XII with Table VIII, page 46, it can be seen that the actual metal contribution from the 0.2-2μ and 2-5μ fractions generally vary from

Table XI

Site of the Highest Concentration of Each Metal
Per Size Fraction of New River Sediment

Metal	105-1000μ	53-105μ	5-53μ	2-5μ	0.2-2μ
Cr	NR1	NR4	NR3	NR2	NR3
Cd	NR4	NR3	NR2	NR4	NR2
Co	NR2	NR4	NR3 and NR4	NR3	All Sites
Cu	NR4	NR3	NR2	NR3	NR3
Ni	NR4	NR3	NR2 and NR3	NR3	NR3
Pb	All Sites	All Sites	All Sites	NR3	All Sites
Zn	NR1	NR3	NR3	NR3	NR3
Mn	NR4	NR4	NR3	NR3	NR3
Fe	NR1	NR2	NR3	NR3	NR3

-=Sites Most Affected by Indian Fork and Unnamed Tributary Immediately South of NR3.

Table XII

Metal Contribution from Each Size Fraction of New River Sediment (in μg/g)

	Cr	Cd	Co	Cu	Ni	Pb	Zn	Mn	Fe
NR1:									
105-1000μ	12	0.67	4.8	6.5	9.7	5.9	21	293	8761
53-105μ	9.1	0.35	4.1	4.1	6.6	3.8	13	55	4261
5-53μ	31	1.2	23	11	22	12	47	235	13,988
2-5μ	7.1	0.28	5.2	2.7	6.5	3.2	14	52	3501
0.2-2μ	5.9	0.33	5.2	2.8	7.1	2.7	14	63	5442
NR2:									
105-1000μ	3.0	0.21	1.7	1.9	3.1	1.7	5.5	87	2462
53-105μ	2.8	0.19	1.6	1.7	2.7	1.6	5.8	21	1869
5-53μ	41	2.1	25	13	33	14	63	231	21,169
2-5μ	31	1.2	22	0.84	26	13	50	227	19,473
0.2-2μ	11	0.67	9.8	5.1	11	4.8	21	170	9650
NR3:									
105-1000μ	24	1.5	11	18	22	14	42	831	20,176
53-105μ	6.7	0.52	3.5	3.5	7.3	3.0	14	60	3255
5-53μ	18	0.97	14	6.2	18	7.3	36	213	10,283
2-5μ	6.2	0.34	5.2	3.2	7.4	3.0	17	114	5486
0.2-2μ	0.8	0.04	0.59	0.43	0.94	0.3	1.9	11	629
NR4:									
105-1000μ	6.4	0.49	3.5	5.0	7.4	3.8	12	232	4690
53-105μ	9.5	0.53	4.9	4.2	7.3	3.9	17	86	4183
5-53μ	39	2.0	31	14	34	16	61	378	17,874
2-5μ	7.8	0.43	5.8	3.0	8.2	3.2	16	114	3673
0.2-2μ	6.1	0.26	5.0	2.7	5.9	2.4	11	87	4568

50% to 400% higher in New River sediments than in Indian Fork sediments. The extreme difference between the two stream systems can be seen by examining the Zn contributions. Zinc contributions from the 0.2-2μ fractions in New River average 10 μg/g of sediment, while the Zn concentrations from the 0.2-2μ fractions of Indian Fork average 2.5μ g/g of sediment. A similar ratio (of about 4:1) of New River's higher contribution of Zn can be seen in the averages of the 5-53μ fractions. In fact, the only fraction of Indian Fork sediment which is higher in Zn contribution (than is New River) is the 105-1000μ size range.

The cause of the above described difference in metal contributions is that the majority of New River sediments are of a finer grain size than are the Indian Fork sediments, Table III, page 36. The 0.2-2μ and 2-5μ fractions of sediment are over twice as abundant in New River sediment than their counterparts in Indian Fork. An increased quantity of these finer grain sizes increases the overall metal content of New River sediment (due to higher metal concentrations in these finer-grained fractions). Table XXVI in the appendix presents the contribution of metals from each size fraction to one gram of sample analyzed.

CHAPTER VI

RESULTS AND DISCUSSION OF X-RAY ANALYSES

The mineralogy of the sediments in the region of sampling is consistent within each size fraction. Regardless of locality, there is no appreciable mineralogic difference between samples in any given size range. There is a transition in mineralogy between the various size fractions. Quartz dominates the coarser material while clay minerals are the major components of the finer-grained sediments. Quartz is not present in detectable amounts in the 0.2-2μ size fraction. The results of all x-ray analyses are presented in Table XIII.

The term "montmorillonite" is used to describe a mineral that gives a 14 Å peak when x-rayed after air drying and whose 14 Å peak collapses to near 10 Å when heated to 550°C. It is believed that the term soil montmorillonite or "montmorillonite" best describes material, as it does not exhibit the same d-spacing (at the 100 intensity peak) that a true montmorillonite exhibits. (Since no secondary peaks for vermiculite were identified, this mineral was not included in the naming of the 14 Å material described above; however, it is quite possible that mixtures of "montmorillonite" and "vermiculite" compose this material.) Also, the 10 Å peak has plateaus or shoulders on the higher d-spacing side. These shoulders indicate an accumulation of mixed-layered clays (interstratified

Table XIII

Results of X-Ray Analyses of Sediments

Sediment Fraction	Minerals Identified
New River, Indian Fork: All Sites	
105-1000μ	Quartz: Dominant Illite Kaolinite "Goethite"
53-105μ	Quartz: Dominant Illite Kaolinite "Goethite" (Very Minor Anglesite Possible in New River Samples)
5-53μ	Quartz: Dominant Illite Kaolinite (Very Minor Anglesite and "Goethite") "Chlorite": Minor
2-5μ	Illite: Dominant Kaolinite: Dominant Quartz Anglesite "Montmorillonite" "Chlorite"
0.2-2μ	Illite Kaolinite "Montmorillonite" "Chlorite"

material). This broadening of the peak base is due to inconsistent internal spacing in the material. Specific investigations to confirm or deny this conclusion should be a portion of a future study.

"Chlorite" is used to describe the presence of a material which could be a stabilized form of weathered illite or simply weathered chlorite. This material exhibits 14-15 Å spacing which remains unaltered when heated to 550°C. The presence of shoulders on the high angle (smaller d-spacing) side of this peak indicates the possible presence of degradation products with a variety of internal spacings.

"Goethite" is used to represent the presence of iron oxides of various oxidation states, thus with possible variations in x-ray diffractograms. This material corresponds closely to true goethite but it may include some siderite that was too scarce to present any strong peaks.

Anglesite has been tentatively identified by the presence of the 100 relative intensity peak and several subsidiary peaks. As previously stated, elevated Pb values in the finer-grained sediment does not correlate with Pb adsorption onto clay surfaces. This strongly suggests the presence of Pb in some discrete chemical form. Elevated $SO_4^{=}$ values in the Indian Fork waters indicate that the fluvial environment may be favorable for the stability of sulfate compounds. Since Pb is not adsorbed to the clays, it probably exists in the form of $PbSO_4$ or some other species not associated with layered silicates.

CHAPTER VII

SUMMARY AND CONCLUSIONS

In analyses of the <1 mm sample, iron levels (averaging 53,000 µg/g) were found to be at least an order of magnitude greater than Mn concentrations (averaging 716 µg/g) which were also at least an order of magnitude greater than most other metals studied. These average values for Mn and Fe approximate the average crustal abundances for these metals, Table V, page 39. Lead and Zn concentrations in the sediment of Indian Fork and New River were at least twice as high as their average crustal abundances. The average crustal concentrations of Zn and Pb were 70 µg/g and 12.5 µg/g, respectively. The average concentration of Zn in Indian Fork sediment was 339 µg/g. Lead had a concentration of 90 µg/g in Indian Fork material, while it averaged 95 µg/g in New River sediment (both concentrations were about eight times the average crustal abundance). The average concentrations of Ni and Cu in sediment from both streams were well below the average crustal abundances of these two metals. The crustal abundance of Cu was 55 µg/g while it was found in levels of about 25 µg/g in the sediment in this study. Nickel has an average crustal abundance of 75 µg/g, but it was only present in an average of 45 µg/g from the New River and Indian Fork sediment. The crustal abundance of Cr was seen to be 25% higher than the average Cr value of 68 µg/g found in the stream's sediment. The average Cd

concentrations in the stream's sediment, 3.5 μg/g, was found to be 1800% higher than its crustal abundance of .2 μg/g. Cobalt concentrations approximated the crustal abundance of 25 μg/g for this metal.

The influx of tributaries into major streams was shown to markedly affect metal content of the entire <1 mm sediment. In the cases of samples IFB, IFC, and IFD the increase in metal content was due to higher concentrations of metals in most of the size fractions of the sediment. In the case of sample NR2 the major reason for the elevated metal content was in increase in the amount of the 0.2-2μ and 2-5μ size ranges. These two fractions were enriched over the coarser sediment in the concentrations of all metals.

A settling phenomena was noticed to occur downstream from tributaries which carried significant amounts of fine material in suspension. This suspended load begins to settle out in the channel of the main stream if that stream has a lower current velocity than the tributary. This settling may account for increased metal content of the sediment at IFC and NR3. Although IFB is downstream from a major tributary to the Indian Fork system, settling is not observed. This process does not occur since the tributary affecting IFB does not contribute large quantities of finer material.

Data from chemical extractions suggested that a large quantity of the metals associated with particulate material was also associated with hydrated iron oxides. On an average, about 40% of each metal was associated with hydrous oxides. Both Mn and Fe were seen to

comprise the major percentage of cations in the category of hydrous oxides. It is, therefore, suggested that these two cations may be the principal metallic ions found in colloidal material in the streams under study. These Fe-Mn colloids were shown to be a significant transporting agent for other trace metals. Copper, Pb and Cr are the only metals which do not appear to be closely associated with hydrous oxides. Further work is necessary to determine the means of concentration of these metals.

It was found that the 0.2-2μ and 2-5μ size fractions contained the highest concentrations of most metals studied. Generally, the coarser fractions had concentrations of metals near their respective abundances in shales. The two finer-grained fractions showed enrichment over the average abundance in shales. Since Cu and Ni were found in levels which only approximated their average sedimentary abundance in the finer-grained material, it is suggested that Ni and Cu are either scarce in the local strata or are preferentially removed from the system.

Data from x-ray diffraction analyses have shown quartz to be dominant in the coarser-grained sediments. The 0.2-2μ and 2-5μ fractions consisted mainly of the clay minerals, kaolinite, illite, "montmorillonite," and "chlorite." "Goethite" and anglesite were also tentatively identified by x-ray diffraction studies.

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LITERATURE CITED

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APPENDIX

APPENDIX

EXTRACTION OF HEAVY METALS FROM SEDIMENTS AND SUBSEQUENT REMOVAL OF METALS ASSOCIATED WITH HYDROUS IRON OXIDES

The following steps delineate the actual procedure followed in this research.

1) Premix solution of 0.3M Na-Citrate (eight parts) + 1.0M HCO_3 (1 part).
2) Place 5.00 g of sample in 50 ml centrifuge tube and add 20 ml of premixed solution.
3) Shake for 16 hours.
4) After shaking, centrifuge at 10,000 r.p.m. for ten minutes to clarify solution.
5) Decant clear supernatant (extract) and store for metal analysis.
6) Add 20 ml of premixed solution to remaining sediment plus 30 g of $Na_2S_2O_4$. Shake for 16 hours.
7) Collect supernatant and store as in Steps 4 and 5.

The above was modified from Jackson, 1956.

ACID DIGESTION PROCEDURE

The following steps delineate the actual procedure followed in this research.

1) Weigh 0.3000 - 0.3200 g of finely ground sample into Teflon beaker.
2) Add 5 ml of concentrated HNO_3 to digest organics. Heat sample in sandbath at 130°C to near dryness. Allow sample to cool slightly.
3) Add 10 ml of 48% HF and 2 ml of concentrated $HClO_4$. Place lid on beaker, covering 80% of the opening.
4) Heat beaker in sandbath at 225°C until sample appears dissolved. (If sample has not dissolved, repeat steps 3 and 4.)
5) Remove lid and evaporate to dryness.
6) Remove beaker from heat and cool slightly.
7) Add 5 ml of 1.0 N HCl and boil gently, for five minutes.
8) Add 5 ml of deionized water and warm again.
9) Transfer solution to 25 ml volumetric flask and bring to correct volume with deionized water.

The above was modified from Jackson, 1958.

DETERMINATION OF CENTRIFUGE TIMES

The following equation is used to calculate time required to effect separation of material using a swinging bucket type centrifuge head.

$$t = \frac{(63.0) \times (10^8) n \log (R/S)}{N^2 \quad D^2 \quad \Delta S}$$

t = sedimentation time in minutes.

n = viscosity of liquid at temperature, T.

R = radius (cm) of rotation at top of sediment.

S = radius (cm) of rotation at surface of suspension.

N = r.p.m.

D = particle diameter in microns.

ΔS = difference in specific gravity of particles and suspension liquid.

Temperature, T, was taken at 20°C.

Particle density was taken to be 2.5 for <0.2μ and 2.65 for 2μ material.

R value allows for sediment of 0.5 cm.

If greater sediment depths are required, change R and recalculate t.

SAMPLE CALCULATION FOR EXTRACTING

µg/g FROM ATOMIC ABSORPTION DATA

$$\mu g/g = \frac{\mu g/ml \text{ (initial volume)(diluted volume)}}{\text{weight of sample}}$$

EXAMPLE. If A.A. data give a µg/ml of 10 (from standard curve) for a 0.3 gram sample analyzed for Fe, and the sample has an initial volume of 25 ml that is diluted 1:100, then proceed as follows:

$$\mu g/g = \frac{(10\ \mu g/ml)(25\ ml)(100\ ml}{0.3\ g}$$

$$\mu g/g = 83,333.$$

OPTICAL DESCRIPTION OF SEDIMENT SIZES >1 mm

The following are descriptions taken from examinations of the material with a binocular microscope.

New River:

NR1: about 60% coal; 40% siltstones and sandstones; all material well rounded.

NR2: about 50% coal; 50% siltstones and sandstones; all well rounded.

NR3: about 50% coal; 30% recent organic (plant) remains; 20% siltstones and sandstones; all lithic material well rounded.

NR4: about 35% coal; a few organic (plant) remains; 65% siltstones and sandstones.

Indian Fork:

IFA: 60% angular coal; 30% rounded siltstones and sandstones.

IFB: 50% angular coal; 50% rounded siltstones and sandstones.

IFC: 60% angular coal; 40% rounded to angular siltstones and sandstones.

IFD: 50% angular coal; 50% rounded to angular siltstones and sandstones.

IFE: 80% coal, very blocky; two limestone fragments, 18% rounded to angular siltstones and sandstones.

PARTICLE SIZE SEPARATION OF STREAM SEDIMENT

The following steps delineate the actual procedure followed in this research.

A) Sieving

1) Wet sieve sample to obtain <1 mm material.
2) Wet seive <1 mm material to obtain 53-1000μ material. Collect and store <53μ material in 1000 ml beaker.
3) Dry the 53-1000μ fraction and dry sieve material to split sample into 53-105μ and 105-1000μ size fractions. Collect and store these fractions.
4) Separate the <5μ material from the <53μ material by gravity sedimentation. Sedimentation of >5μ material requires 5 cm fall in 37 minutes and 30 seconds at 20°C. Decant and store liquid and repeat several times.
5) Collect and store 5-53μ sediment from previous step.

B) Centrifugation (using RC2-B Superspeed Centrifuge)

1) Take suspension of <5μ material and fill the 250 ml bottles to a depth of 9 cm as measured from the same surface on which the bottle is sitting.
2) Securely cap the bottles. Shake the bottles thoroughly, place them in an HS-4 centrifuge rotor, and begin centrifugation immediately after shaking.
3) Centrifuge bottles for 13 minutes at 500 r.p.m.
4) Carefully decant supernatent into a container marked <.2μ.

5) Resuspend sediment in bottles to same depth as before with deionized water and centrifuge as before.

6) Repeat Step 5 at least two additional times, or until separation is completed.

7) Resuspend sediment as above and centrifuge at 750 r.p.m. for five minutes to settle material >2μ.

8) Collect supernatent in a container marked 0.2-2μ material.

9) Repeat Steps 7 and 8 at least two additional times, or until separation is complete.

10) Residue in bottle is 2.5μ material.

The above was modified from Jackson, 1956.

Table XIV

Results of Selected Triplicate Analyses
of Indian Fork Sediment in µg/g

	Cr	Cd	Co	Cu	Ni	Pb	Zn	Mn	Fe
IFB 53-105µ:									
1	59	2.7	22	22	55	41	69	786	49,600
2	58	1.2	28	19	43	33	70	713	27,100
3	57	3.2	34	18	42	25	75	656	27,500
Average	58	2.4	28	20	47	33	71	718	34,700
IFC 5-53µ:									
1	54	4.1	34	5	47	33	127	940	57,300
2	59	1.3	38	22	51	33	110	958	39,200
3	55	4.1	43	23	47	25	119	777	39,800
Average	56	3.2	38	17	48	30	119	892	45,300
IFD 2-5µ:									
1	115	6.2	62	32	93	70	168	1908	71,600
2	123	3.1	194	39	127	54	166	1763	70,600
3	123	5.2	104	47	104	50	174	2215	72,700
Average	120	4.8	120	39	108	58	169	1962	71,700
IFE 105-1000µ:									
1	59	3.9	26	20	51	45	90	979	41,000
2	67	3.1	26	24	48	41	99	968	39,700
3	68	3.7	32	30	51	37	99	1217	38,900
Average	65	3.6	28	25	50	41	96	1055	39,800
IFA <1 mm:									
1	58	3.2	32	24	42	81	130	713	46,200
2	*	3.1	32	25	41	82	164	697	45,100
3	52	2.9	46	19	45	73	102	893	39,200
Average	55	3.1	37	23	43	79	132	768	43,500
IFC <1 mm:									
1	78	3.2	37	31	41	99	174	827	58,600
2	*	2.9	41	27	41	115	205	968	68,100
3	77	3.3	47	24	48	98	146	931	65,700
Average	78	3.1	42	27	43	104	175	909	64,200
IFE <1 mm:									
1	51	2.9	29	19	42	50	166	746	37,300
2	*	2.9	37	19	43	33	172	720	35,200
3	58	2.9	47	20	59	41	132	857	31,300
Average	55	2.9	38	19	48	41	157	774	34,500

* Not Analyzed.

Table XV

Results of Selected Triplicate Analyses of
New River Sediment in µg/g

	Cr	Cd	Co	Cu	Ni	Pb	Zn	Mn	Fe
NR1 5-53µ:									
1	67	2.5	49	23	54	27	99	493	31,300
2	67	2.7	48	23	41	27	102	527	29,600
3	70	3.1	34	24	48	27	103	519	31,200
Average	68	2.8	44	23	48	27	101	513	30,700
NR2 5-53µ:									
1	83	4.1	49	26	66	27	126	466	41,400
2	76	4.2	47	26	61	28	121	439	41,600
3	78	3.7	49	27	69	27	125	465	42,700
Average	79	4.0	48	26	65	27	124	457	41,800
NR3 2-5µ:									
1	106	5.8	97	53	128	52	296	1920	94,400
2	106	5.8	82	56	125	49	293	2003	94,800
3	96	5.8	103	58	135	52	292	1927	97,000
Average	103	5.8	94	56	129	51	294	1950	95,400
NR4 .2-2µ:									
1	119	5.2	104	56	120	50	228	1819	95,200
2	126	5.6	103	56	126	50	227	1820	95,100
3	118	5.8	97	56	119	54	218	1782	98,700
Average	121	5.5	101	56	122	51	224	1807	96,400
NR1 <1 mm:									
1	67	2.5	33	25	45	83	207	481	35,600
2	*	2.9	37	25	42	82	181	533	41,800
3	64	2.8	33	31	41	71	189	554	34,200
Average	66	2.7	34	27	43	79	192	523	37,200
NR3 <1 mm:									
1	59	4.2	29	32	42	83	232	705	42,300
2	*	4.2	33	29	43	82	246	696	44,200
3	55	4.6	29	32	43	74	221	653	49,600
Average	57	4.3	30	31	43	80	233	685	45,400

* Not Analyzed.

Table XVI

Data From Intralab Comparison Analyses

Sample	Cr	Co	Cd	Cu	Ni	Pb	Zn	Mn	Fe
				Schrader:					
1	34	17	3.2	15	30	25	60	437	29,920
2	38	27	3.3	17	27	22	58	790	35,066
3	62	31	4.2	25	47	30	71	748	87,354
4	38	24	2.8	20	38	37	81	706	45,278
5	53	41	2.7	30	69	36	133	911	70,388
6	28	25	2.7	17	47	27	79	439	32,263
				Upham:					
1	26	22	2.0	14	30	37	47	733	49,658
2	32	16	2.0	15	38	28	49	487	263,066
3	62	33	3.4	20	63	40	83	748	85,335
4	26	32	2.0	18	40	36	58	715	48,366
5	41	32	2.3	31	76	44	93	807	67,574
6	17	15	1.6	14	29	32	48	447	33,946

Table XVII

Percentages of Total Metals Associated
With Hydrous Iron Oxides

	Cr	Cd	Co	Cu	Ni	Pb	Zn	Mn	Fe
IFA	14	60	35	12	26	*	#	78	60
IFB	16	65	37	13	27	*	#	65	51
IFC	12	50	37	14	27	*	#	74	54
IFD	20	60	52	20	30	*	#	81	55
IFE	16	60	35	15	23	*	#	75	58
NR1	12	50	21	12	17	*	#	44	60
NR2	11	44	16	13	13	*	#	47	55
NR3	15	45	26	10	19	*	#	38	70
NR4	10	60	20	10	17	*	#	37	55

* Below Limits of Detection.

Indeterminable Due to Reagent Contamination.

Table XVIII

Metal Concentrations from First Analysis of <1mm Material (in μg/g)

	Cr	Cd	Co	Cu	Ni	Pb	Zn	Mn	Fe
IFA	58	3.1	32	25	41	82	164	697	45,081
IFB	87	3.5	37	32	49	130	243	1159	91,543
IFC	78	2.9	41	27	41	115	205	968	68,055
IFD	44	2.9	25	19	33	98	171	636	51,353
IFE	51	2.9	37	19	43	33	172	720	35,165
NR1	67	2.9	37	25	42	82	181	533	41,831
NR2	87	4.5	53	31	66	164	705	573	71,265
NR3	59	4.2	33	29	43	82	246	696	44,190
NR4	77	3.3	40	29	42	42	208	665	42,387

Table XIX

Metal Concentrations from Second Analysis of <1mm Material (in μg/g)

	Cr	Cd	Co	Cu	Ni	Pb	Zn	Mn	Fe
IFA	52	3.2	32	24	42	81	130	713	46,176
IFB	*	4.2	41	33	49	131	214	1062	93,137
IFC	77	3.2	37	31	41	99	174	827	58,697
IFD	*	3.2	27	22	33	83	166	729	43,889
IFE	58	2.9	29	19	42	50	166	746	37,276
NR1	64	2.5	33	25	45	83	207	481	35,631
NR2	*	4.8	48	31	66	160	726	559	71,839
NR3	55	4.2	29	32	42	83	232	705	42,303
NR4	*	3.2	33	27	43	66	206	635	42,024

* Not Analyzed.

Table XX

Metal Content of Indian Fork Sediment from First Replicate Analysis of Size Fractions (in µg/g)

	Cr	Cd	Co	Cu	Ni	Pb	Zn	Mn	Fe
IFA									
105-1000µ	57	2.7	26	17	54	33	77	1226	38,910
53-105µ	39	2.7	15	17	40	33	62	588	52,998
5-53µ	39	6.6	32	5	41	33	66	456	47,201
2-5µ	103	6.2	68	38	94	66	207	1747	120,811
0.2-2µ	107	4.2	83	52	112	92	237	1471	91,514
IFB									
105-1000µ	67	4.1	27	27	77	56	137	1407	83,241
53-105µ	59	2.7	22	22	55	41	69	786	49,652
5-53µ	52	4.2	37	5	45	33	68	705	51,410
2-5µ	95	7.1	92	38	99	69	222	2165	76,617
0.2-2µ	147	4.1	45	58	99	91	274	1693	97,434
IFC									
105-1000µ	51	3.4	29	16	60	39	84	1168	47,391
53-105µ	39	2.7	15	16	51	41	66	520	52,728
5-53µ	54	4.1	34	5	47	33	127	940	57,227
2-5µ	117	6.9	69	52	94	71	227	2399	101,376
0.2-2µ	131	4.1	25	52	99	90	204	1624	114,905
IFD									
105-1000µ	46	4.1	25	16	58	39	80	983	50,191
53-105µ	55	3.5	15	11	53	40	64	479	59,180
5-53µ	68	5.6	37	5	35	45	121	748	76,463
2-5µ	115	6.2	62	32	93	70	168	1908	71,642
0.2-2µ	114	4.1	111	46	100	91	205	1520	102,627
IFE									
105-1000µ	59	3.9	26	20	51	45	90	979	41,009
53-105µ	36	3.1	15	11	37	41	64	522	48,045
5-53µ	55	4.1	28	5	45	36	111	908	56,106
2-5µ	90	7.7	62	32	93	57	190	2203	42,271
0.2-2µ	121	5.4	61	69	105	90	192	2291	73,554

Table XXI

Metal Content of Indian Fork Sediment from Second Replicate Analysis of Size Fractions (in µg/g)

	Cr	Cd	Co	Cu	Ni	Pb	Zn	Mn	Fe
IFA									
105-1000µ	46	3.0	27	19	45	33	86	1069	36,740
53-105µ	36	0.82	25	15	33	37	58	534	25,469
5-53µ	52	1.2	30	21	41	33	118	471	26,943
2-5µ	109	4.1	78	38	115	53	186	1553	114,454
0.2-2µ	105	5.1	128	52	110	74	245	1463	73,554
IFB									
105-1000µ	71	3.9	27	25	67	42	145	1387	81,811
53-105µ	58	1.2	28	19	43	33	70	713	27,049
5-53µ	55	2.1	40	22	58	33	95	720	29,485
2-5µ	116	4.5	77	46	119	53	184	2024	72,887
0.2-2µ	138	5.7	121	57	134	74	238	1680	82,760
IFC									
105-1000µ	54	3.0	28	19	47	32	85	1172	46,865
53-105µ	45	0.82	28	15	33	33	68	597	25,696
5-53µ	59	1.3	38	22	51	33	110	958	39,189
2-5µ	129	5.8	124	49	126	54	208	2205	99,967
0.2-2µ	156	8.8	66	68	118	55	202	1576	94,133
IFD									
105-1000µ	46	2.3	26	17	45	33	85	908	47,855
53-105µ	46	1.6	25	21	40	33	67	468	27,094
5-53µ	82	2.1	53	25	65	41	112	751	41,254
2-5µ	123	3.1	194	39	127	54	166	1763	70,692
0.2-2µ	125	5.1	93	46	97	82	202	1483	86,491
IFE									
105-1000µ	67	3.1	26	24	48	41	99	968	39,709
53-105µ	36	1.6	28	15	41	33	67	507	22,891
5-53µ	59	1.2	40	26	70	33	109	497	28,127
2-5µ	86	4.6	143	46	125	40	156	2145	39,293
0.2-2µ	108	4.2	66	83	98	70	239	2246	56,148

Table XXII

Metal Content of New River Sediment from First Replicate Analysis of Size Fractions (in μg/g)

	Cr	Cd	Co	Cu	Ni	Pb	Zn	Mn	Fe
NR1									
105-1000μ	63	3.2	25	31	48	28	104	1410	42,458
53-105μ	62	2.5	30	28	47	27	94	372	31,137
5-53μ	67	2.5	49	23	54	27	99	493	31,260
2-5μ	109	4.1	78	41	98	50	204	779	52,805
0.2-2μ	111	6.2	93	53	132	52	274	1180	103,614
NR2									
105-1000μ	47	3.2	29	27	47	27	79	1354	38,244
53-105μ	51	3.7	30	31	47	27	110	375	33,110
5-53μ	83	4.1	49	26	66	27	126	466	41,418
2-5μ	113	4.1	79	30	92	48	178	811	69,560
0.2-2μ	115	7.2	104	51	115	50	229	1802	103,959
NR3									
105-1000μ	40	2.5	19	26	39	27	70	1530	38,920
53-105μ	59	4.1	31	30	62	27	113	564	29,311
5-53μ	67	3.2	32	23	66	27	133	785	39,010
2-5μ	106	5.8	97	53	128	52	286	1920	94,417
0.2-2μ	126	5.8	105	68	153	50	306	1820	107,438
NR4									
105-1000μ	44	3.7	25	29	54	27	83	1625	33,394
53-105μ	68	3.9	34	31	54	28	104	605	29,940
5-53μ	68	3.2	55	23	58	27	96	656	29,890
2-5μ	119	5.8	78	41	112	44	248	1560	51,155
0.2-2μ	119	5.2	104	56	120	50	228	1819	95,199

Table XXIII

Metal Content of New River Sediment from Second Replicate Analysis of Size Fractions (in μg/g)

	Cr	Cd	Co	Cu	Ni	Pb	Zn	Mn	Fe
NR1									
105-1000μ	54	3.1	21	30	43	27	94	1375	40,984
53-105μ	67	2.5	27	30	47	27	92	410	29,732
5-53μ	67	2.7	48	23	41	27	102	527	29,557
2-5μ	106	4.3	80	41	98	46	203	809	53,279
0.2-2μ	113	6.1	102	52	134	49	267	1202	101,725
NR2									
105-1000μ	46	3.3	25	31	40	27	93	1358	38,690
53-105μ	47	2.9	25	29	48	28	96	352	32,468
5-53μ	76	4.2	47	26	61	28	121	439	41,597
2-5μ	107	4.4	79	30	88	41	182	812	69,536
0.2-2μ	113	6.9	103	56	118	51	222	1823	101,362
NR3									
105-1000μ	52	3.1	21	41	42	27	90	1605	37,215
53-105μ	63	3.2	33	33	69	27	133	530	29,871
5-53μ	63	3.9	52	23	64	27	133	789	37,166
2-5μ	106	5.8	82	56	125	49	293	2003	14,759
0.2-2μ	125	7.1	94	73	159	49	331	1818	102,135
NR4									
105-1000μ	47	3.2	25	42	52	27	90	1684	33,604
53-105μ	67	3.7	35	28	50	27	133	624	29,811
5-53μ	63	3.6	50	23	56	27	112	623	30,700
2-5μ	97	6.2	82	41	115	44	203	1610	50,870
0.2-2μ	126	5.6	103	56	126	50	227	1820	95,136

Table XXIV

pH Values and Water Temperatures at Sampling Sites

Site	pH	Temperature in °C
New River		
1	6.0	10
2	6.0	10
3	6.0	10
4	6.0	10
Indian Fork		
A	6.1	10.5
B	6.1	11.0
C	6.1	11.0
D	6.0	11.0
E	6.6	11.0
Lick Branch	5.5	11.0

Table XXV

Metal Contribution from Each Size Fraction of Indian Fork Samples, in μg/g of Sample

	Cr	Cd	Co	Cu	Ni	Pb	Zn	Mn	Fe
IFA									
105-1000μ	30.2	1.7	15.4	10.3	28.5	18.8	46.7	654	21,560
53-105μ	12.2	0.3	3.6	2.9	6.7	6.3	10.8	101	7062
5-53μ	9.7	0.8	6.5	2.7	8.6	6.9	19.3	97	7785
2-5μ	2.2	0.1	1.5	0.8	2.2	1.3	4.2	35	2470
0.2-2μ	1.8	0.1	1.8	0.8	1.9	1.4	4.1	25	1403
IFB									
105-1000μ	51.8	3.0	20.3	19.5	54.	36.8	10.6	1048	61,895
53-105μ	0.3	0.1	1.7	1.5	3.4	2.6	4.8	52	2646
5-53μ	7.4	0.5	5.5	2.0	7.3	4.6	11.5	100	5663
2-5μ	3.0	0.2	2.4	1.2	3.1	1.7	5.7	59	2093
0.2-2μ	2.0	0.1	1.2	0.8	1.6	1.2	3.6	24	1261
IFC									
105-1000μ	35.0	2.1	19.	14.5	35.6	23.8	56.1	772	31,105
53-105μ	6.7	0.3	3.5	3.5	6.7	5.9	10.8	88	6290
5-53μ	9.1	0.4	5.8	2.2	7.8	5.3	19.0	152	7713
2-5μ	2.3	0.1	1.8	1.0	2.1	1.2	4.1	44	1913
0.2-2μ	2.6	0.1	0.8	1.1	1.9	1.3	3.7	29	1881
IFD									
105-1000μ	39.1	2.7	22.1	14.5	44.2	30.6	70.6	804	41,670
53-105μ	1.4	0.1	0.6	0.5	1.3	1.0	1.9	13	1208
5-53μ	5.3	0.3	3.2	1.1	3.6	3.1	8.3	53	4179
2-5μ	4.5	0.2	4.9	1.4	4.2	2.4	6.4	70	2704
0.2-2μ	1.7	0.1	1.0	0.6	1.4	1.2	2.9	21	1324
IFE									
105-1000μ	51.	2.8	21.0	17.8	40.5	34.8	77.0	789	32,691
53-105μ	2.7	0.2	1.7	1.0	3.0	2.8	5.0	39	2696
5-53μ	4.3	0.2	2.6	1.2	4.4	2.7	8.4	53	3201
2-5μ	1.7	0.1	2.0	0.7	2.1	0.9	3.3	41	775
0.2-2μ	1.8	0.1	1.0	1.2	1.6	1.3	2.5	36	1038

Table XXVI

Metal Contribution from Each Size Fraction of New River Samples, in μg/g of Sample

	Cr	Cd	Co	Cu	Ni	Pb	Zn	Mn	Fe
NR1									
105-1000μ	13.6	0.7	5.3	7.1	10.6	6.4	22.8	320	9596
53-105μ	9.8	0.4	4.4	4.4	7.1	4.1	14.0	59	4565
5-53μ	33.5	1.3	24.5	11.5	24.	13.5	50.5	255	15,205
2-5μ	7.7	0.3	5.6	2.9	7.0	3.4	14.5	564	3766
0.2-2μ	6.4	0.4	5.6	3.0	7.6	2.9	15.5	68	5852
NR2									
105-1000μ	3.0	0.2	1.7	1.9	3.1	1.7	5.5	87	2462
53-105μ	2.8	0.2	1.6	1.7	2.7	1.6	5.8	21	1869
5-53μ	40.0	2.1	24.0	13.0	32.0	14.0	62.0	227	20,754
2-5μ	30.8	1.2	22.1	8.4	25.5	12.6	50.4	227	19,473
0.2-2μ	10.7	0.7	9.8	5.1	11.0	4.8	21.2	170	9650
NR3									
105-1000μ	25.3	1.5	11.0	18.7	22.6	14.9	44.0	862	20,937
53-105μ	6.7	0.5	3.5	3.5	7.3	3.0	13.5	60	3255
5-53μ	18.2	1.0	14.6	6.4	18.2	7.6	37.2	220	10,665
2-5μ	6.4	0.4	5.4	3.3	7.6	3.1	17.6	118	5675
0.2-2μ	0.8	0.04	0.6	0.4	0.9	0.3	1.9	11	629
NR4									
105-1000μ	6.4	0.5	3.5	5.0	7.4	3.8	12.2	232	4690
53-105μ	9.5	0.5	4.9	4.2	7.3	3.9	16.7	86	4183
5-53μ	39.6	2.0	31.8	13.8	34.2	16.2	62.4	384	18,177
2-5μ	7.8	0.4	5.8	3.0	8.2	3.2	16.4	114	3673
0.2-2μ	6.0	0.3	5.1	2.7	6.0	2.5	11.2	89	4663

VITA

Edward Leon Schrader was born in Vicksburg, Mississippi, on June 19, 1951. He received his elementary and secondary education in the public school of Long Beach, Mississippi. He was graduated from Long Beach High School in June of 1969. In August, 1969, he entered Millsaps College in Jackson, Mississippi where he was awarded the David Martin Key Merit Scholarship. He was graduated cum laude with a Bachelor of Science degree in Geology in June, 1973.

He entered the Graduate School of the University of Tennessee in August, 1973, and served as a teaching assistant during the time of his enrollment. He received the Master of Science degree with a major in Geology in June, 1975. He is a member of Sigma Gamma Epsilon and the Society of Economic Geologists.

He is married to the former Myra Lee Ladner of Gulfport, Mississippi.