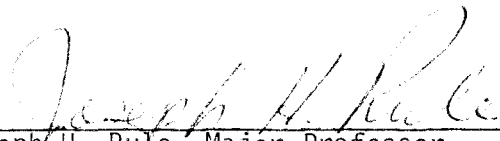
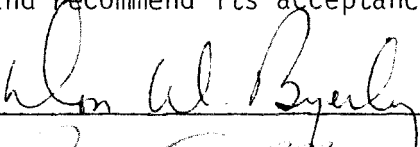
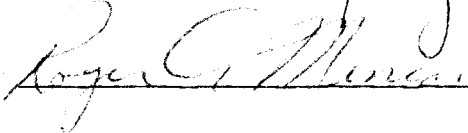


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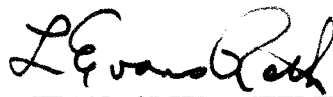
I am submitting herewith a thesis written by Richard H. Ketelle entitled "Characteristics of the Mineral and Metal Content of Suspended Sediment, New River Basin, Tennessee." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Geology.


Joseph H. Rule, Major Professor

We have read this thesis
and recommend its acceptance:

Accepted for the Council:


Vice Chancellor
Graduate Studies and Research

CHARACTERISTICS OF THE MINERAL AND METAL CONTENT OF
SUSPENDED SEDIMENT, NEW RIVER BASIN,
TENNESSEE

A Thesis
Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

Richard H. Ketelle
August 1977

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ACKNOWLEDGEMENTS

The author wishes to acknowledge everyone who made contributions to this research and made the study possible. Financial support of this project was supplied by the Energy Research and Development Agency (ERDA) on Research Grant No. E-(40-1)-4946.

The writer wishes to thank Dr. Rule, Committee Chairman, for his advice and direction of the research. The valuable advice and critical review of this manuscript provided by Dr. Byerly and Dr. Minear is greatly appreciated.

Bernard Fredrick of the USGS Division of Water Resources deserves thanks for supplying stream flow data from the Bill's Branch and Indian Fork gaging stations.

Appreciation is expressed to other researchers on this project for their valuable discussions with the author and exchange of information obtained in their investigations in the New River Basin.

ABSTRACT

Large volume (80 liter) water samples were collected from five sites on four streams in the New River Basin of Tennessee for study of the suspended sediment. Parameters selected for investigation were:

- (1) Sediment size distribution
- (2) Mineral composition of the sediment
- (3) Metal content of the sediment
- (4) Extractable Fe-Mn Oxide content of the sediment
- (5) Association of heavy metals with Fe-Mn oxides

Sediment was separated by gravity settling and continuous flow centrifugation. Size separations showed that most of the sediment was in the 2-5 μ m size range and 0.2-2 μ m particles were second most abundant in most samples regardless of the degree of surface disturbance in the watershed. Streams in extensively mined watersheds carried heavier loads of suspended sediment than a stream in an unmined watershed.

The most abundant minerals in the suspended sediment in this region were quartz, kaolinite, and illite. Chlorite, vermiculite, lepidocrocite, and mixed layer clays were identified as minor components of the sediment. Fe and Mn oxides were found to be important as a cementing agent of flocculated particles and tended to obscure size distinction of the clay minerals. Chlorite content of argillaceous bedrock was higher than that of the sediment indicating that weathering processes allowed vermiculite to form in soils.

Sediment was analyzed for Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn by

atomic absorption following total acid digestion using hydrofluoric and perchloric acids. Analysis of size separated samples showed that levels of most metals increased with decreasing particle size. Mn tended to accumulate in the coarser size fractions of the sediment. Fe, Mn, and Zn levels were higher in mined watersheds than in unmined watersheds. Other metals were present in about the same levels in suspended sediment from all streams sampled. Assessment of the total suspended load in each stream would indicate that a higher total volume of metals is carried in the sediment in mined watersheds than in unmined watersheds.

High levels (>50 weight percent) of dithionite extractable Fe and Mn oxides were found in sediment from an extensively mined watershed and lower levels were found in streams less affected by mining. Levels of extractable oxides corresponded with total Fe content of size separated samples and increased with decreasing particle size.

Acid extraction of Fe and Mn oxides and analysis of the extract solutions showed that the Zn content of the sediment was strongly associated with Fe content and Co and Cu were associated with Fe but to a lesser extent. Analysis of residues remaining after this extraction showed that Cr, Ni, and Pb were nearly evenly distributed between acid extractable forms and residue materials.

This study showed that coal mining affects the suspended sediment by increasing levels of Fe, Mn, and Zn; which are present in oxide precipitates. Suspended sediment load is increased by mining activities with a resulting increase in the total metal volume transported in suspended particulates. Vermiculite content of suspended sediment in mined

watersheds was lower than in unmined watersheds. Bulk mineralogy was little affected by mining but formation of oxide coatings on sediment particles was heavier in mined watersheds than in unmined areas.

TABLE OF CONTENTS

SECTION	PAGE
I. INTRODUCTION	1
Purpose of the Investigation	2
II. SCOPE AND BACKGROUND	3
Plan of Study	3
Location	5
Previous Investigations	5
Geologic Setting	8
Heavy Metal Levels in Bedrock	11
III. PHYSICAL AND MINERALOGICAL CHARACTERIZATION OF SUSPENDED SEDIMENT	13
Sediment Size Distribution	13
Methods Used for Mineral Identification	15
Results of X-ray Diffraction Analyses	17
Summary of Mineralogy	24
Conclusions	25
IV. HEAVY METAL CONTENT OF SUSPENDED SEDIMENT	26
Total Metal Content of Bulk Samples	27
Variations in Metal Content	31
Metal Content of Size Separated Sediment	33
Extractable Fe-Mn Oxide Content of Sediment	36
Association of Heavy Metals with Fe-Mn Oxides	38
Effect of Mining Activities on Suspended Sediment	42

SECTION	PAGE
Conclusions	44
V. SUMMARY	46
BIBLIOGRAPHY	50
APPENDIX	54
VITA	71

LIST OF TABLES

TABLE	PAGE
1. Heavy Metal Content of Rock and Soil Materials	12
2. Mineral Content of Suspended Sediment	22
3. Metal Content Data	28
4. Mean Metal Content and Range of Mean Metal Content of Suspended Sediment In Each Stream Over the Study Period . .	32
5. Metal Content of Size Separated Samples Collected 4/2/76	34
6. Results of Fe Extraction and Residue Analyses	41
7. Sediment Size Distribution Data	58
8. Metal Content of Sediment (6/29/76 and 7/12/76)	59
9. Metal Content of Sediment (9/28/76)	60
10. Diffraction Data from Indian Fork Samples	66
11. Diffraction Data from Fe Extracted Samples from Indian Fork . .	67
12. Diffraction Data from Bill's Branch Samples	68
13. Diffraction Data for Samples from New River below Indian Fork	69
14. Diffraction Data for Fe Extracted Sediment from New River below Indian Fork	70

LIST OF FIGURES

FIGURE	PAGE
1. Location Map Showing the Upper New River Basin	6
2. Stratigraphic Column of Pennsylvanian Rocks in the Study Area	9
3. Sediment Size Distribution Histograms for Samples Collected 9/28/76	14
4. X-ray Diffraction Peak Intensities of 4.26Å, 7Å, and 10Å Peaks for Size Separated Samples	20
5. Metal Content of Each Size Fraction of Suspended Sediment from Four Streams (4/2/76)	35
6. Extractable Oxide Content of Bulk Samples from Five Sample Sites	37
7. Extractable Oxide Content of Size Separated Suspended Sediment Samples from Three Streams	39
8. X-ray Diffraction Patterns from 0.2-2 µm Sediment from Bill's Branch. A = Untreated; B = Glycolated; C = Heat Treated	62
9. X-ray Diffraction Patterns from 0.2-2 µm Sediment from Indian Fork. A = Untreated; B = Glycolated; C = Heat Treated	63
10. X-ray Diffraction Patterns from Cave Branch Sediment. A = Untreated; B = Heat Treated	64
11. X-ray Diffraction Patterns from a Dark Shale Sample. A = Untreated; B = Glycolated; C = Heat Treated	65

I. INTRODUCTION

Studies of the mineralogical and chemical character of suspended sediment in fluvial systems are scarce and only within the past decade have detailed works been published. Sediment carried in suspension constitutes a significant fraction of the total material eroded by and transported in major river systems. Judson (1968) estimated that the annual suspended load of rivers draining all the continents is about 10 billion tons of sediment. Other workers report higher estimates than Judson's figure.

Suspended sediment is an integral part of the fluvial system and as such undergoes interactions with the stream and river water. The clay rich material has a high ion exchange capacity and may interact with ions in solution by absorbing them onto exchange sites (Kennedy, 1965). Some organic molecules present in the fluvial system as natural components or as contaminants may also be associated with clay minerals. Another important interaction between suspended particulates and the aqueous system is that of nucleation of hydrous oxides of Fe and Mn on sediment. In areas where coal mining is common the weathering of pyrite may allow large amounts of dissolved Fe and Mn to be carried into streams where oxidation causes precipitation of hydrous Fe-Mn oxides. The resulting floc may be very important as an ion exchange medium for metals in solution once it has formed. Coprecipitation of other metals in solution may also occur when the Fe precipitates leading to formation of an Fe precipitate rich in other metals (Jenne, 1968).

Accelerated physical and chemical weathering of bedrock and soil materials disturbed by mining operations causes a rise in suspended particulates and dissolved metals in streams. Investigation of mineralogy and metal content of suspended sediment is necessary to understand fully the stream chemistry and distribution of heavy metals within the fluvial system.

Purpose of The Investigation

The present study was an outgrowth of research on the effects of surface mining for coal on groundwater and surface water flow regimes, water quality, and stream sediment metal content in small watersheds. The purpose of investigating the suspended sediment was to characterize the mineral content of the sediment, to determine the levels of heavy metals present in the sediment, and to determine heavy metal content of different size fractions of sediment. In addition to general characterization of mineralogy and heavy metal content of the sediment this study was intended to assess the impact of surface mining on mineralogy and heavy metal content of suspended sediment.

II. SCOPE AND BACKGROUND

Plan of Study

Large volume (80 liter) water samples were collected and the suspended sediment was removed by centrifugation using a Sorvall RC2-B superspeed centrifuge with a continuous flow system. Size separation was done by gravity settling for particles $>5\mu\text{m}$ diameter and by continuous flow centrifugation for particle $<5\mu\text{m}$ diameter. Flow rate and rotor speeds for continuous flow separations were determined empirically using clay suspensions which were separated by conventional centrifugation on the same machine. The size fractions used were those of Jackson (1956): $>20\mu\text{m}$ =coarse silt, $5\text{--}20\mu\text{m}$ =fine silt, $2\text{--}5\mu\text{m}$ =coarse clay, $0.2\text{--}2\mu\text{m}$ =medium clay, $<0.2\mu\text{m}$ =fine clay.

Following size separation the samples were dried in a low temperature oven (40°C), weighed, and a sediment distribution histogram was plotted. A mineralogical analysis of sediment in each size fraction was made using X-ray diffraction techniques. Details of the X-ray diffraction procedures are presented later. Mineralogy of argillaceous bedrock was determined and was compared with the mineralogy of suspended sediment in the sample streams to determine similarities of the two materials. Mineralogy of the sediment from all the streams sampled was compared to determine any differences in sediment mineralogy between disturbed and undisturbed watersheds.

Total metal content of the sediment was determined by analysis of unseparated samples and by calculation of weighted averages of the metal

content in each size fraction in size separated samples. Heavy metal content of sediment in all the streams sampled was compared to note any effects of surface disturbance on metal content. Metal content of the clay size bottom sediment in the control stream was used as a background since this stream (Lowe Branch) which was used as the control stream for other investigations in this project, yielded insufficient suspended sediment for analytical work. Sediment from each size fraction was subjected to complete acid digestion using an HF-HClO₄ digestion procedure. After digestion the samples were analyzed to determine metal content of each size fraction and trends of metal content as a function of particle size. Chemical extraction of hydrous Fe-Mn oxides was done on selected samples, both size separated and unseparated, to measure the amount of extractable Fe-Mn oxides and to show tendencies of heavy metals to accumulate in the oxides or in the clay minerals. Residues which remained after oxide extraction were acid digested and analyzed for metal content and results were compared with data from analysis of the oxide materials.

The metals which were selected for analysis in this study were Co, Cr, Cu, Fe, Mn, Ni, Pb, and An. Previous investigation (Rule, 1976) of heavy metal content of bottom sediment in this area showed that other elements such as Hg and As which are important as toxic elements were not present in significant levels in this area. All analyses for metal content were done by atomic absorption using a Perkin-Elmer model 403 atomic absorption spectrophotometer.

Location

The study area for this research is in the Cumberland Mountains of Tennessee. All sample streams are tributaries of the New River. Sample sites used in this study are indicated on the location map (Figure 1). Sample streams were Indian Fork, New River above and below the Indian Fork confluence, Bill's Branch, and Cave Branch. Sample sites were located at the lower end of small rapids in an attempt to obtain homogeneous samples representing the entire channel.

Coal mining has been extensive using both surface and underground methods in the Indian Fork watershed and reclamation of old mines has been poor. Many mines, both surface and underground, have operated in the New River watershed above the Indian Fork confluence. Sampling of New River above and below Indian Fork was done to evaluate the contribution of metals by sediment from Indian Fork to the New River suspended sediment.

A surface mine was operated in the Bill's Branch watershed in 1975 and was completed and reclaimed prior to initiation of this study. Control data were obtained from suspended sediment in Cave Branch and from clay size bottom sediment in Lowe Branch. Cave Branch has been logged with minimal surface disturbance and no surface mining has been done in the watershed. Lowe Branch has not been mined and no recent logging activities have occurred and consequently suspended sediment sampling produced insufficient sample for analysis.

Previous Investigations

There are few publications on suspended sediment in fluvial

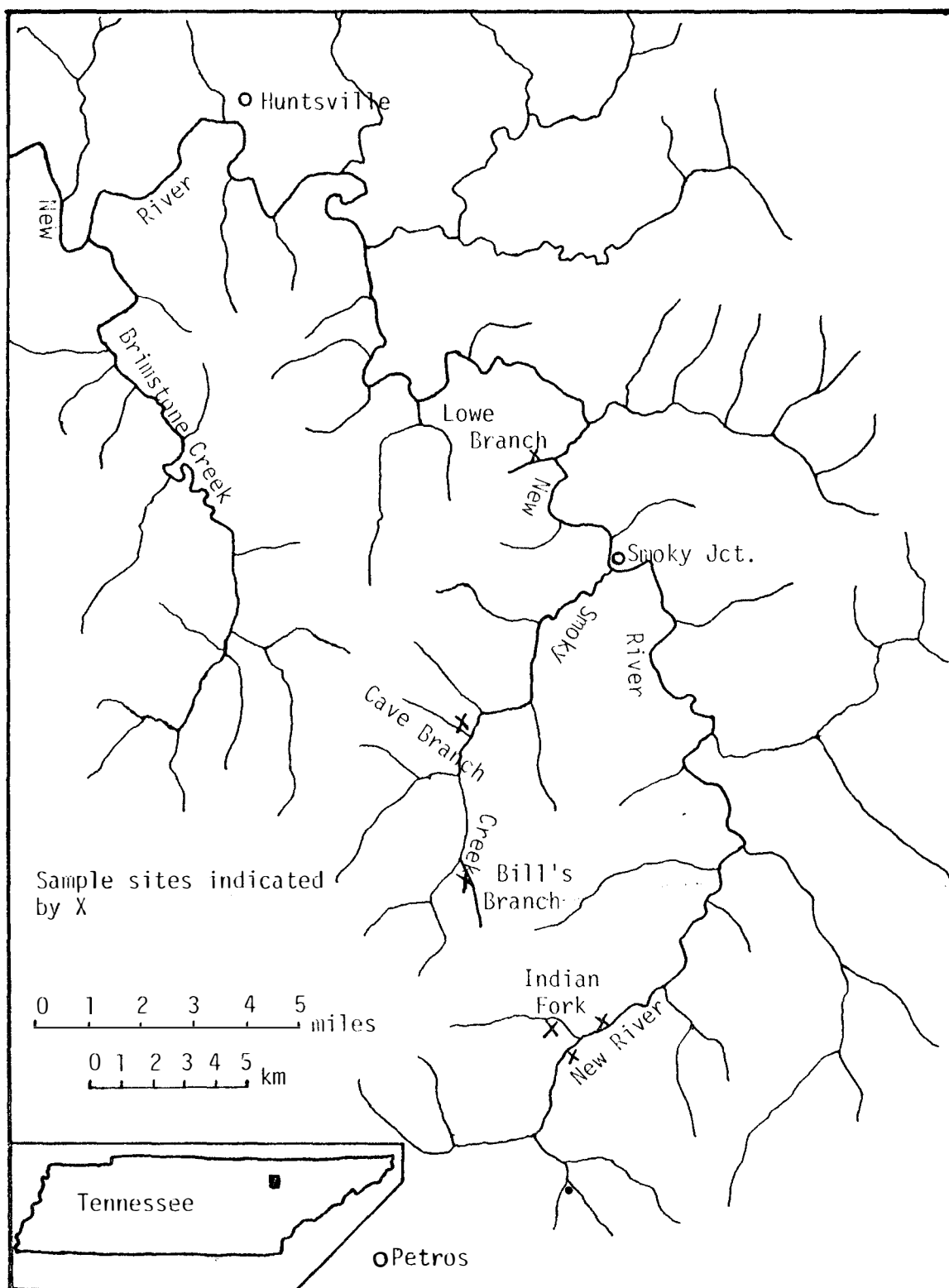


Figure 1. Location map showing the Upper New River Basin.

systems and the majority of published articles deal with mineralogy and ion exchange capacity. Kennedy (1965) presented data on quantitative mineral content and cation exchange capacity of stream sediment from 21 streams throughout the United States. Mineralogy of suspended sediment in the Maumee River Basin, Ohio was reportedly by Wall and Wilding (1976). They found that illite (mica), quartz, and chlorite-vermiculite were the dominant minerals in the suspended sediment and that seasonal and downstream variations in the sediment mineralogy were minor. Neiheisel and Weaver (1967) reported the mineral content of sediment in rivers, estuaries, and offshore areas of South Carolina and Georgia. Their investigation showed that kaolinite was the major clay mineral in rivers originating on the Piedmont and smectite was the major clay mineral in rivers of the Coastal Plain. Distinct clay and heavy mineral suites were found in rivers draining the two types of source area. Mineralogy and Fe, Mn, and Pb content of suspended sediment in selected Kansas streams were reported by Angino et al. (1974). They found that smectite, illite, and kaolinite were the major clay minerals in suspended sediment. Their mineralogical data compared favorably with that presented by Kennedy (1965) for the Kansas River at Wamego. They found Fe levels comparable to those of bedrock materials and Mn levels were elevated with respect to bedrock Mn levels.

Data on metal content of fluvial suspended sediment were given in Turekian and Scott (1967), Gibbs (1973), Angino et al. (1969), and Carpenter et al. (1975). Conclusions drawn from these papers regarding suspended sediment chemistry were:

- (1) heavy metal content of suspended sediment is highly variable

(as much as 200% variation at a single sample site on different sample dates)

- (2) metal content of sediment does not vary directly with stream flow
- (3) association of Co, Cu, Ni, and Zn with Fe-Mn oxide coatings is significant
- (4) the major transport mechanisms of metals in fluvial systems are in oxide coatings and in crystalline sediment with transport in organic phases and in solution being much less important.

It is believed that the present study is the first investigation of mineralogy and metal content of suspended sediment in the coal fields of East Tennessee. Supportive information on mineralogy and metal content of bottom sediment in the streams sampled in this study was available in previous work by Schrader (1975) and Upham (1975). Data on metal content of soils and Pennsylvanian shales from Kentucky were available in USGS Professional Paper 574-F by Connor and Shacklette (1975). Heavy metal levels in bedrock materials in this study area were available in theses by Franks (1957) and Thompson (1977).

Geologic Setting

The study area lies in the Wartburg Basin; a structural basin in the northern Cumberland Plateau where the thickest section of Carboniferous age rocks in Tennessee are located. Rocks of the northern Cumberland Plateau in East Tennessee are of Middle Pennsylvanian age. The oldest outcropping rocks in the New River Basin are in the Slatestone Group and the youngest rocks in the area are in the Cross Mountain Group. The stratigraphic section (Figure 2) shows a sequence of alternating dark shales and mudstones interbedded with sandstones and coals.

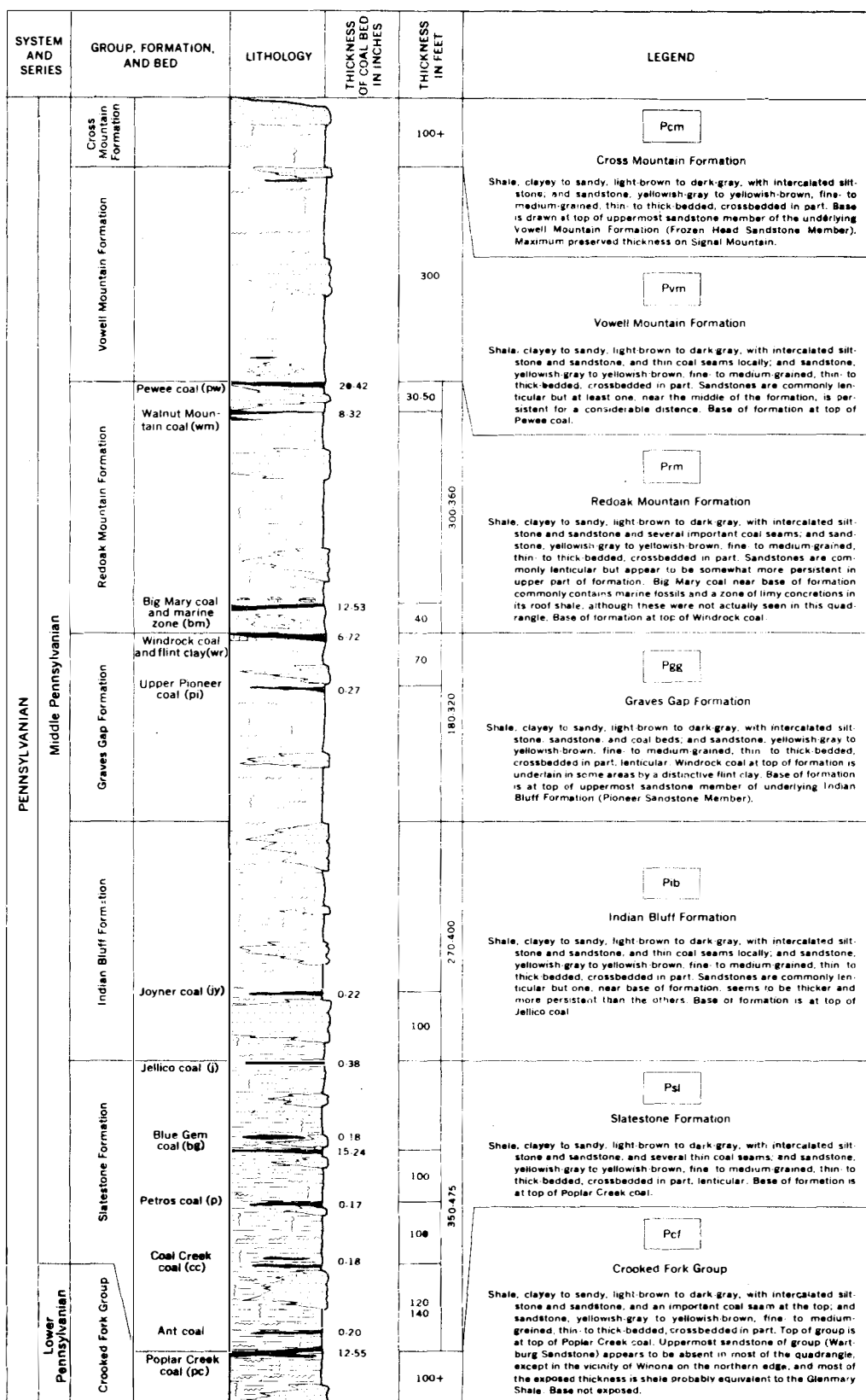


Figure 2. Stratigraphic column of Pennsylvanian rocks in the study area (from Luther and Avery, 1970).

Shales and mudstones with interbedded coal beds predominate in the lower part of the section and sandstones become thicker and more predominant in the upper part of the section. Many coals outcrop in this area and at least five (Jellico, Windrock, Big Mary, Walnut Mountain, and Pewee) have been surface mined in the study area.

The paleoenvironmental model developed by Ferm (1974) for Pennsylvanian sediments in the Appalachian Plateaus region indicates that these sediments were deposited in a huge deltaic complex. Detailed paleoenvironmental mapping by Briggs (1976) in the study area supports this hypothesis and shows that the shales and mudstones were deposited in interdistributary bays and the sandstones were deposited by migrating distributary channels and splays from these channels. Reducing conditions produced by decay of organic matter in the sediment at the time of deposition and the presence of sulfur, especially in areas where marine waters encroached on the lower delta plain, allowed formation of pyrite in the shales and mudstones. Pyrite is present as disseminated framboidal pyrite in the shales and mudstones (Caruccio and Ferm, 1974) and as massive sulfide accumulations several centimeters in dimension which are evident in some fresh exposures of shale and coal. Oxidation of pyrite upon exposure to water and air in the weathering horizon is the source of acid in groundwaters and results in solution of Fe, Mn, and other metal ions which are carried into the surface streams. High levels of acid production were encountered only locally in bedrock pH determinations published by the Environmental Protection Agency (1976) for samples collected in this general area. Carbonate minerals are present in the rocks as ironstone concretions and as shell material

deposited in marine zones. These materials may play an important role in neutralization of acid produced by pyrite oxidation.

The zone of oxidation of bedrock is generally several meters in depth in this area but soils developed are thin on the steep slopes which prevail in the area. Soils are silty, slightly acid, and are low in plant nutrients. Soils in valley bottoms are thicker than on the slopes but are also silty and acid. Disturbed soils in this area are readily leached of plant nutrients and are susceptible to rapid erosion. Revegetation of disturbed soils in this area is often slow due to the low soil nutrient content and erosion problems occur especially where hillside soils are disturbed.

Heavy Metal Levels in Bedrock

The abundance of the metals of interest in this study in rock and soil materials from various sources is shown in Table 1. Included in the table are values for average crustal abundance, Pennsylvanian shales from Kentucky and Missouri, soils from southeastern Kentucky, the average for B horizon soils in the Eastern U.S., shales from this study area, and metals extractable from strip mine spoil bank material from Kentucky. The data for Pennsylvanian dark shales from Kentucky, Missouri, and from this study area show that background levels for these metals in this region are higher than levels in both the average crustal abundance and the B horizon average for the Eastern U.S. The elevated background levels of metals in the rock and soil materials is of importance because chemical weathering releases part of the total metal content to the groundwater and eventually to the surface waters.

TABLE 1
Heavy Metal Content of Rock and Soil Materials
($\mu\text{g/g}$ except Fe)

Element	A	B	C	D	E	F	G	a	H b	c
Cd	0.8	<1-5	<1-5	NR	3.2	NR	<1	NR	NR	NR
Co	19	8-71	2-20	NR	37	64	7	10	8.4	7.6
Cr	90	35-230	70-150	NR	225	125	14	60	76	78
Cu	45	NR	5-100	85	27	54	36	13	20	19
Fe %	4.82	0.45-10	0.91-8.4	3.75	3.0	4.7	1.5	2.1	4.2	4.3
Mn	850	12-1000	30-500	1800	432	380	290	600	170	140
Ni	68	<10-83	10-70	122	103	95	13	13	20	20
Pb	20	<20-53	<10-100	NR	38	38	14	17	12	15
Zn	95	<500-780	25-130	145	134	135	36	27	36	33

NR=not reported

A--Average crustal abundance (Ahrens, 1968)

B--Kentucky Pennsylvanian shales (Connor and Shacklette, 1975)

C--Pennsylvanian shales from Missouri (Connor and Shacklette, 1975)

D--Highest concentration in extract solution from spoil material
(Massey and Barnhisel, 1972)

E--Mean metal content for shales and mudstones from this study area
(Franks, 1975)

F--Black shale from this study area (Thompson, 1977)

G--Average for B horizon soil, Eastern U.S. (Connor and Shacklette, 1975)

H--a, b, and c horizon values for southeastern Kentucky soil
(Connor and Shacklette, 1975)

III. PHYSICAL AND MINERALOGICAL CHARACTERIZATION OF SUSPENDED SEDIMENT

Sediment Size Distribution

Histograms plotted from weights of size separated and dried samples were used to show the sediment size distribution for suspended sediment in this study. A representative histogram for each sample site is shown in Figure 3. The histograms show that the 2-5 μ m class was the model class and the 0.2-2 μ m class was usually the second ranking class and other classes were subordinate. This relationship held for the majority of samples which were size separated. Variations in flow conditions between low and moderate flow produced no major shift in the sediment distribution histograms. Size distribution data for high flow conditions were not obtained. Additional size distribution data are included in the Appendix.

Samples collected and separated by conventional centrifugation prior to use of the continuous flow centrifuge system showed a tendency for the 5-20 μ m class to predominate. This variation reflects the differences in the two methods of separation. Separation of particles by centrifugation results in the formation of a sediment cake in the bottom of the centrifuge vessel. Resuspension of the sediment involves disaggregation of the packed sediment. When working with clays and fine particles, which tend to flocculate, it is impossible to resuspend the sediment without disaggregating some particles which, in the stream environment, may have been flocculated. Mineralogical studies often

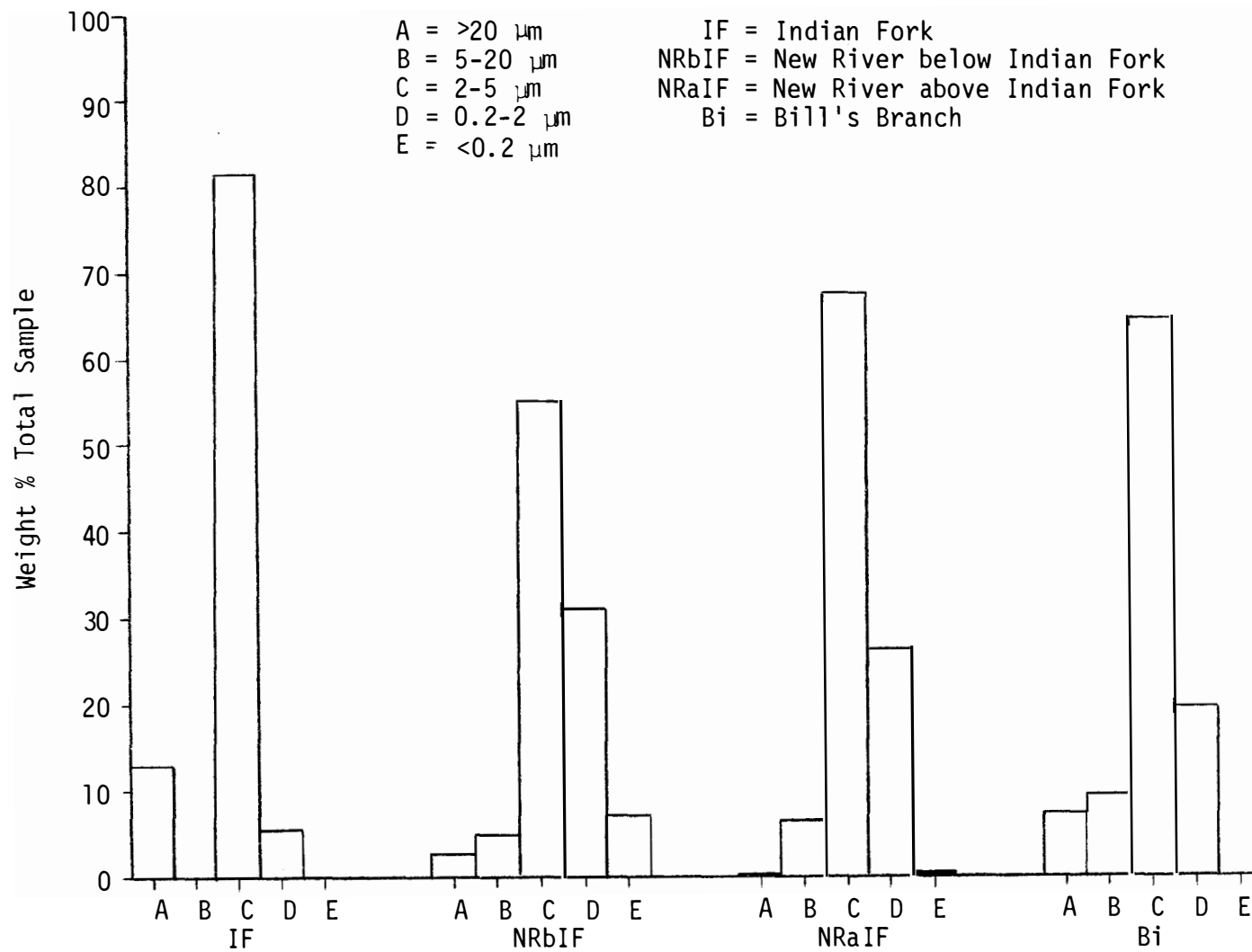


Figure 3. Sediment size distribution histograms for samples collected 9/28/76.

involve addition of a deflocculant to the sediment to disperse the particles but since samples collected for this study were to be analyzed for metal content as well as mineral content no chemical dispersants were used. Samples separated by continuous flow centrifugation were disaggregated in the centrifuge tubes on a vortex mixer and resuspended in deionized water. Samples separated by conventional centrifugation were disaggregated in centrifuge bottles on a mechanical shaker. It is not possible to determine whether the vortex mixer treatment disaggregated particles which were flocculated in the stream environment or whether the mechanical shaker failed to disaggregate particles which were packed together during centrifugation.

Methods Used for Mineral Identification

Mineral composition of the suspended sediment was determined by X-ray diffraction using Ni filtered Cu radiation on a Phillips-Norelco diffractometer. The X-ray tube was operated at 35 Kv and 17 mA and the detector scan speed was $1^{\circ} 2\theta$ per minute. Two elutriated slides were prepared from each size fraction after size separation. One slide was treated with ethylene glycol and X-rayed when freshly dried and the other was X-rayed after being air dried, then it was heat treated and X-rayed a second time. Acid treatment and KCl saturation were applied to selected samples when adequate sample volume was available. Diffraction patterns were run from 2° to $30^{\circ} 2\theta$ as diagnostic peaks for the minerals present are observed in that range.

The suspended sediment in this area was found to be a mixture of quartz, kaolinite, illite, chlorite, vermiculite, lepidocrocite, and

mixed layer clays. Criteria used for mineral identification were:

- (1) Quartz--presence of a peak at $4.26\text{\AA}$
- (2) Kaolinite--presence of a peak at $7.1\text{-}7.2\text{\AA}$ which disappeared with heating to 550°C for 1 hour
- (3) Illite--presence of a peak at $10.0\text{-}10.2\text{\AA}$
- (4) Chlorite--presence of a peak at $14\text{\AA}$ which persisted with heating to 550°C for 1 hour
- (5) Vermiculite--presence of a peak at $14\text{\AA}$ which disappeared with heating to 550°C for 1 hour
- (6) Lepidocrocite--presence of a peak at $6.25\text{-}6.3\text{\AA}$ which disappeared with heat treatment or was absent after Fe extraction
- (7) Mixed layer clays--presence of peaks with spacings greater than $19\text{\AA}$

These criteria were outlined in Lucas (1962), Jackson (1956), Carroll (1970) and others and are the diffraction characteristics commonly used in routine mineral identification in soils and sediments.

Diffraction patterns obtained from these samples were complex due to the mixture of minerals present and the effects of hydrous Fe and Mn oxides which can prevent clay particles from lying flat on the slides and can attenuate the X-ray beam. Comparison of diffraction patterns obtained from samples after extraction of Fe-Mn oxides with those from unextracted samples showed that peak intensities increased by about a factor of two after oxide coatings were removed. This was attributed to more uniform orientation of particles and reduced beam attenuation as mentioned by Dion (1945). Identification of clay minerals present was complicated by superposition of peaks for more than one mineral at the

same d-spacing. The (001) peak for chlorite and the (002) peak for vermiculite both occur at about $14\text{\AA}$ and heat treatment was used to collapse the vermiculite to about $10\text{\AA}$ leaving the chlorite peak at $14\text{\AA}$. The $7\text{\AA}$ peak seen in these patterns had contributions from the (001) peak of kaolinite, the (002) chlorite peak, and the (004) vermiculite peak. Again heating was used to remove the kaolinite and vermiculite contributions to this peak and generally only a weak peak produced by chlorite was seen.

The $10\text{\AA}$ illite peak was usually asymmetric toward larger d-spacings and the presence of $10\text{-}14\text{\AA}$ "intergrade" material was noted in most samples. The "intergrade" material may result from partial hydration of illitic material or partial collapse of vermiculitic material. Heat treatment destroyed this material with a resulting sharpening and intensification of the $10\text{\AA}$ peak indicating that dehydration collapsed the spacing to a uniform $10\text{\AA}$.

Saturation of samples with ethylene glycol showed that there was not a significant amount of smectite in the stream sediment in this area. KCl saturation to collapse vermiculite to $10\text{\AA}$ was not effective in these samples as noted by lack of a systematic decrease in intensity of the $14\text{\AA}$ peak following saturation. Fe and Mn oxides either within the interlayer areas or as surface coatings may have prevented the collapse.

Results of X-ray Diffraction Analyses

Comparison of diffraction patterns from Indian Fork, New River above and below Indian Fork, and Bill's Branch samples showed that the

bulk mineralogy was the same for all four sites on three streams. Minerals identified were quartz, kaolinite, illite, chlorite, vermiculite, lepidocrocite, and 10-14⁰Å intergrade material. Some mixed layer minerals were indicated by occurrence of large spacing peaks. Specific mixed layer minerals were not identified because of low intensities of the large spacing peaks however a recurring peak at 21-23⁰Å may indicate that alleverdite was present in some samples. Clay mineral peak intensities were generally higher in samples from Bill's Branch than from the other streams; possibly because of lower Fe oxide content in this sediment as noted by visual inspection and chemical analysis. X-ray analysis of unseparated samples from Cave Branch showed the same mineral content as was found in the other streams in the area. The 14⁰Å mineral in Cave Branch was predominantly vermiculite while both chlorite and vermiculite were present in sediment in New River above Indian Fork. Bedrock disturbances in strip mining allow rapid weathering of shales and mudstones which contribute chlorite to the clay fractions in stream sediment in Bill's Branch, Indian Fork, and New River. The high vermiculite content of sediment in Cave Branch indicates that during more thorough weathering in the soil profile the chlorite weathers to vermiculite. Soils and groundwaters in the area are slightly acid and chlorite is less stable than kaolinite or illite in acid conditions. Inspection of samples with a microscope showed that coal was a minor component of all samples. The mineral assemblage found in suspended sediment in this study was qualitatively the same as that found in rocks of Pennsylvanian age in the Illinois Basin by Glass (1956) and was very similar to the mineral assemblage found in suspended sediment in the Eastern United States as

reported by Kennedy (1965).

No detailed quantitative analysis of the mineral composition of the sediment studied here was undertaken (i.e. density separation or selective dissolution techniques) due to the very small samples available and the complexity of the mineral mixture. X-ray diffraction peak intensities are difficult to use as a good quantitative measure of mineral content however comparison of peak intensity for specific minerals in different size fractions taken from one sample can show trends of mineral segregation on a size basis. Peak intensities of the 4.26 $\text{\AA}$ quartz peak, the 10 $\text{\AA}$ illite peak, and the 7 $\text{\AA}$ peak were plotted for each size fraction to show semiquantitative trends of mineral composition (Figure 4). Data are presented for size separated samples from Indian Fork, New River below Indian Fork, and Bill's Branch (Cave Branch and New River above Indian Fork yielded insufficient sample for analysis after size separation). Interpretation of this diagram must be restricted to relative mineral abundance between size fractions within a single stream sample and no valid inferences can be made relating peak intensity to quantitative mineral content in samples from different streams.

Quartz content increased in the coarser size fractions in each stream as would be expected. The 10 $\text{\AA}$ and 7 $\text{\AA}$ peaks showed the same general trends which may indicate that most of the clay minerals tend to have the same size distribution or that flocculation of the clay particles has obscured any size differentiation of the clays. Data for Indian Fork showed that 14 $\text{\AA}$, 10 $\text{\AA}$, and 7 $\text{\AA}$ peaks had their greatest intensities in the 2-5 μm fraction while in Bill's Branch the maximum for

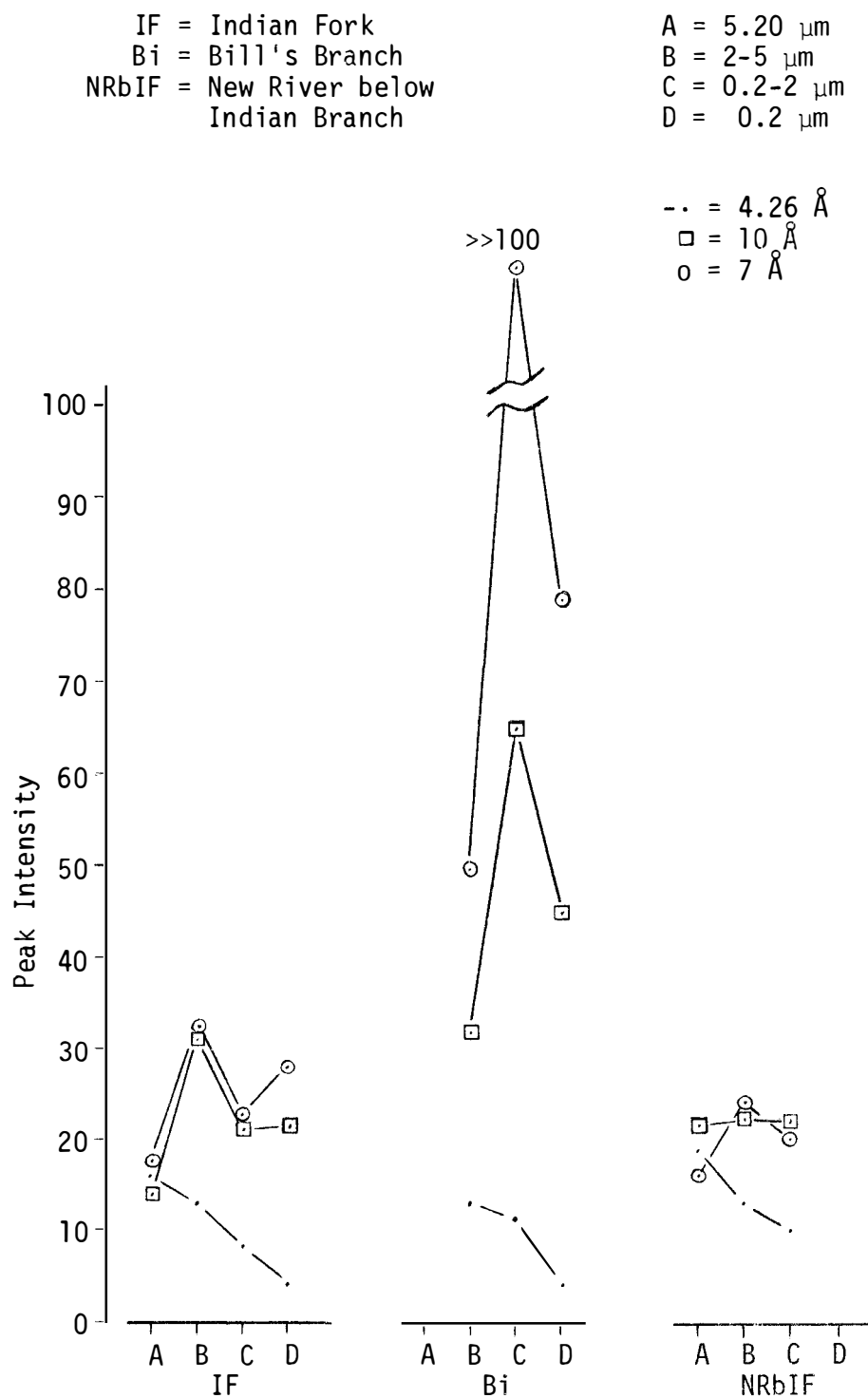


Figure 4. X-diffraction peak intensities of 4.26 $\text{\AA}$, 7 $\text{\AA}$, and 10 $\text{\AA}$ peaks for size separated samples.

these peaks was in the 0.2-2 μ m fraction. This difference is probably due to flocculation of clay particles and cementation by Fe oxide in Indian Fork resulting in larger particles which are an aggregate of smaller particles.

Table 2 shows the general trends of mineral abundance in each size fraction. Quartz dominated the coarsest size fractions (as determined by visual inspection with a microscope) and decreased in abundance with decreasing particle size. Kaolinite and illite were the dominant clay minerals in the sediment and they dominated all the clay size fractions. Stronger reflections were seen from mixed layer minerals in the <0.2 μ m fraction than in the other clay fractions but the overall importance of these minerals in the sediment was minor. Vermiculite and chlorite were subordinate components of the clay and were minor components of the coarser sediment. Lepidocrocite never assumed more than minor importance in the X-ray patterns though more than 50 weight percent of the sediment in Indian Fork may be hydrous Fe oxide. Freshly formed oxides of Fe and Mn are generally thought to be amorphous (Jenne, 1968) and thus would not produce an X-ray diffraction peak. The lepidocrocite peak observed may have been produced by concretionary Fe oxide or oxide formed in the soil.

A bottom sediment sample from Indian Fork was Fe extracted and the residue was size separated and eluted onto slides to determine whether any of the clay minerals tended to occur in a particular size range after the Fe oxide coatings were removed. A mixed layer clay with basal spacing of 30.0-30.5 $\text{\AA}$ was detected in the <0.2 μ m and 0.2-2 μ m classes but was absent in the 2-5 μ m class. This peak had greatest

TABLE 2
Mineral Content of Suspended Sediment

Size Fraction	Mineral Content	
5-20 μm	Quartz	Dominant
	Kaolinite)	Subordinate
	Illite)	
	Chlor. + Verm.)	Minor
	Mixed Layer)	
2-5 μm	Kaolinite)	Dominant
	Illite)	
	Quartz	Subordinate
	Chlor. + Verm.)	
	Mixed Layer	Minor
0.2-2 μm	Kaolinite)	Dominant
	Illite)	
	Quartz	Subordinate
	Chlor. + Verm.)	
	Mixed Layer	Minor
0.2 μm	Kaolinite)	Dominant
	Illite)	
	Chlor. + Verm.)	Subordinate
	Mixed Layer)	
	Quartz	Minor

Dominant- peak intensity >50 @ scale of 100

Subordinate- peak intensity 10-50 @ scale of 100

Minor- peak intensity <10 @scale of 100

Intensity in the 0.2 μ m class. The 14 $\text{\AA}$ peak of chlorite + vermiculite was detected in all three size fractions and its intensity increased with decreasing particle size. The 10 $\text{\AA}$ illite peak grew broader and more intense with decreasing particle size. Maximum intensity of the 7 $\text{\AA}$ peak was seen in the 0.2-2 μ m fraction. The 4.26 $\text{\AA}$ quartz peak was minor in the 0.2 and 0.2-2 μ m fractions and increased in intensity significantly in the 2-5 μ m fraction.

Diffraction patterns obtained from samples of dark shales and mudstones collected on highwall exposures showed that the mineral composition of the argillaceous bedrock was very similar to that of the suspended stream sediment. The shales and mudstones were composed of quartz, kaolinite, illite, chlorite, minor vermiculite and mixed layer minerals. No lepidocrocite peaks were observed in diffraction patterns from shales and mudstones. An important difference between patterns from bedrock samples and those from sediment samples was the behavior of the 14 $\text{\AA}$ peak with heat treatment. A strong 14 $\text{\AA}$ peak remained in patterns for shales and mudstones after heating at 550° C, indicating that most of the 14 $\text{\AA}$ mineral was chlorite while a decrease in intensity of this peak in sediments indicated that some vermiculite was present. Comparison of data from bedrock clays with clays from streams having varying degrees of surface disturbance showed a progressive increase in vermiculite content with more thorough weathering of the clays. A progressive decrease in chlorite content and an increase in vermiculite content was seen in comparing the mineralogy of bedrock shales--> stream sediment in a surface mined basin--> stream sediment in a basin with only soil disturbance.

Summary of Mineralogy

The mineral content of the suspended sediment from all the streams sampled varied little. Kaolinite and illite were the major clay minerals identified in the area. Chlorite was the dominant 14Å mineral identified in the argillaceous bedrock and a weathering reaction was identified wherein chlorite was transformed to vermiculite with the aid of acidic groundwater in the weathering horizon. Streams draining watersheds which have been surface mined typically had both chlorite and vermiculite in the clay fractions while a stream in a watershed which has had only minor surface disturbance carried mostly vermiculite as the 14Å mineral. Mixed layering of clays was observed with probably more than one variety being present; however mixed layer clays comprised a minor portion of the total suspended sediment load.

Hydrous Fe and Mn oxides are a significant component of suspended sediment in this area; especially in Indian Fork. Lepidocrocite was identified as the crystalline form of FeO(OH) present though much of the freshly precipitated flocculant may be amorphous. Determination of the amount of crystalline vs. amorphous oxides present in the samples was not attempted. Hydrous oxides are precipitated on the surface of sediment particles and can act as a cementing agent bonding together fine clay particles into coarser particles which, in the natural system, may settle more rapidly than the original clay particles in suspension. Removal of Fe oxide coatings before size separation and analysis showed that kaolinite was generally coarser grained than the other clays and that particle size enlargement by the oxides can obscure the size distinction of the clay minerals.

Conclusions

Several general statements can be made regarding the effects of mining activities on the physical and mineralogical parameters of suspended sediment.

- (1) Streams in surface mined watersheds carry heavier sediment loads than streams in slightly disturbed or undisturbed watersheds.
- (2) The size distribution of suspended sediment is not significantly affected by varying degrees of surface disturbance in small watersheds.
- (3) The amount of hydrous Fe-Mn oxide in suspension is dependent upon mining activity within a watershed. The source of this material is chemical weathering of sulfides. Surface mine spoil and deep mine and auger mine drainage contribute dissolved Fe and Mn to surface water.
- (4) Much of the oxide rich sediment contributed to New River by Indian Fork settles out downstream during normal flow forming accumulations of Fe rich sediment in the bottoms of pools; periodic flushouts of these accumulated sediments during high flow are expected to result in significant variations in suspended sediment chemistry.
- (5) Bedrock disturbance results in accelerated physical weathering of rock materials which changes the mineralogy in upper soil horizons. Vermiculite in the soils of an undisturbed watershed may be an important ion exchange medium and may scavenge metal ions out of groundwater. Disturbed soils contain less vermiculite and ionic mobility is expected to be higher in disturbed areas than in undisturbed areas.

IV. HEAVY METAL CONTENT OF SUSPENDED SEDIMENT

In order to characterize the heavy metal content of suspended sediment several types of treatments were necessary. Metal content was determined on bulk or unseparated samples to establish the average metal content of suspended sediment in each stream. Distribution of metals as a function of particle size was determined by digestion and analysis of size separated samples. Samples for these total metals analyses were digested in an HF-HClO₄ treatment. The weight percent of extractable Fe-Mn oxides was determined by using a citrate-dithionite extraction procedure. This procedure was intended for use in determination of heavy metal associations with the Fe-Mn oxides but analysis of the extract proved unsatisfactory. A 1 N HCl extraction procedure was used to determine the levels of extractable metals and affinities of heavy metals for the Fe-Mn oxides. Metal content of the extracted material was compared with that of the residue remaining after the extraction. The effect of mining on suspended sediment metal content was inferred by comparison of heavy metal content of suspended sediment from each sample site with metal content of clay size bottom sediment from an undisturbed control stream.

Sediment samples were analyzed for Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn by atomic absorption methods using a Perkin-Elmer model 403 spectrophotometer. Atomic absorption analysis for these elements is generally free of interferences but nonspecific absorption may occur when analyzing solutions high in dissolved solids using analytical

wavelengths less than 250 nm. A deuterium background corrector was used to minimize this potential interference. Analysis of coal fly ash (Reference Material #1633) obtained from the National Bureau of Standards (NBS) showed that the accuracy of analyses in this work was within 5% of metals content reported by the NBS with the exception of Pb which was 22% lower than the reported value.

Total Metal Content of Bulk Samples

Metal content of unseparated sediment samples from each of five sample sites on two sample dates is shown in Table 3. Also shown are total metal contents of size separated sediment as determined by calculation of the weighted average of data obtained from analyses of each size fraction (Table 3, Section B) and weighted average data from Fe extraction analyses (Table 3, Section C). Comparison of metal content of suspended sediment with background levels in bedrock (data from Franks, and Thompson, Table 1, page 12) indicated that metal content in suspended sediment was similar and bedrock for most metals. Fe, Mn, and Zn were present in suspended sediment in levels much greater than background concentrations. An association between Fe and Zn content was indicated in these data. Associations between Fe and Mn content and Mn and Zn content were poor. Co, Cu, and Ni, which often show an association with Fe and Mn content in stream sediment (Carpenter, 1975), Jenne 1968) did not always show this association in these samples.

Fe content showed a consistent pattern when metals data from the different sample sites were compared. The streams were ranked according to Fe content which showed Indian Fork > (New River below Indian Fork) >

TABLE 3

Metal Content Data
($\mu\text{g/g}$ except Fe)

Date	Site	Co	Cr	Cu	Fe-%	Mn	Ni	Pb	Zn
<u>A. Total Metals Data</u>									
3/21/77	IF	37	181	69	23.9	824	119	22	780
"	NRaIF	35	120	52	5.3	770	81	46	249
"	NRbIF	30	130	63	11.0	708	85	38	409
"	Bill	17	136	36	3.7	639	42	25	152
"	CB	69	58	76	5.5	734	29	63	187
5/2/77	IF	48	90	57	17.1	839	112	22	598
"	NRaIF	32	166	64	5.2	723	89	79	333
"	NRbIF	25	137	71	14.4	474	50	35	373
"	Bill	19	105	37	4.0	487	44	36	173
"	CB	23	136	80	4.7	698	45	68	205
<u>B. Data from weighted averages from size separated samples</u>									
4/2/76	IF	23	96	93	13.2	453	72	17	148
"	NRaIF	16	190	49	5.8	677	76	27	199
"	NRbIF	11	120	62	13.6	456	73	14	388
"	Bill	14	65	79	7.6	506	51	15	ND
6/29/76	IF	92	112	68	18.0	900	146	14	575
"	NRaIF	102	203	192	10.8	1199	90	10	600
"	NRbIF	80	99	142	21.4	463	119	13	451
7/12/76	IF	94	146	109	29.6	923	161	7	569
"	NRaIF	107	ND	465	13.4	1112	267	33	ND
"	NRbIF	91	209	230	26.7	730	176	14	589
"	Bill	66	192	70	4.6	657	95	16	193
9/28/76	IF	37	112	116	15.1	412	ND	43	586
"	NRaIF	38	107	81	3.4	660	107	37	256
"	NRbIF	103	128	105	5.6	988	134	10	335
"	Bill	25	164	84	4.3	764	79	46	294
<u>C. Data from weighted averages from acid extracted samples</u>									
3/1/77	IF	23	140	56	19.6	473	94	33	540
"	NRaIF	21	204	87	6.7	510	128	44	341
"	NRbIF	17	116	90	15.5	426	76	59	452
"	Bill	23	51	49	4.3	729	47	43	161
"	CB	21	100	70	5.5	636	45	34	289

TABLE 3 (Continued)

Date	Site	Co	Cr	Cu	Fe-%	Mn	Ni	Pb	Zn
4/11/77	IF	26	125	36	24.7	586	92	33	878
"	NRaIF	23	179	148	6.7	429	63	47	741
"	NRbIF	15	65	109	21.4	551	35	48	580
"	Bill	41	97	57	4.8	558	37	57	244
<u>D. Average metal content of Lowe Branch clay size sediment</u>									
		63	227	94	5.6	479	97	57	288

IF-Indian Fork

NRaIF-New River above Indian Fork

NRbIF-New River below Indian Fork

Bill-Bill's Branch

CB-Cave Branch

(New River above Indian Fork) > Bill's Branch. Fe content in some samples from Cave Branch exceeded that of Bill's Branch but Fe content in Cave Branch sediment was not consistently higher or lower than that of Bill's Branch. No similar systematic trend was apparent in the data for other metals in this study. Locally the Fe content reflected the severity of soil and bedrock disturbance due to mining as indicated by the consistently high values in Indian Fork. Over a larger area the effect was diminished as noted by the relatively low Fe content of sediment in New River above Indian Fork even though there are other localized areas of severe disturbance in that area of the watershed. A previous investigation of bottom sediment in this area showed little correlation between metals content and mining activity (Upham 1975) but this study showed at least a local increase in Fe and Zn content of suspended sediment which was related to severity of bedrock disturbance by mining.

Average metal content for clay size particles in bottom sediment in Lowe Branch, an unmined, undisturbed stream, are presented in Table 3 (Section D). Comparison of data from Lowe Branch bottom sediment with data from suspended sediment from the other sample sites showed that Fe, Mn, and Zn contents were higher in suspended sediment from disturbed watersheds than in the fine sediment of the control stream. Co, Cr, Cu, Ni, and Pb generally showed lower concentrations in suspended sediment from disturbed watersheds than in fine fractions from the control stream.

Variations in Metal Content

Mean total metal content and range of total metal content of sediment at each sample site over the entire study period were determined (Table 4). Comparison of heavy metal data for Indian Fork and New River above and below Indian Fork showed that sediment metals levels in New River above Indian Fork were about the same as or higher than levels in Indian Fork and in New River below Indian Fork. This trend held for all metals analyzed except Fe and Zn which were highest in Indian Fork. Indian Fork was a source of Fe and Zn in sediment of New River but was only a minor source of other metals when compared to other sources upstream on the New River.

The range of values for each metal at each sample site was great and cause-effect relationships cannot be defined using available data. Stream flow data for Bill's Branch and Indian Fork were obtained from the USGS and metals content was compared to flow data. No direct correspondence between flow data and metal content of suspended sediment was evident. Co, Cu, and Ni values in Table 3 showed a slight increase in low flow summer samples while Pb showed a slight decrease in those samples. This is a general relationship and it is probable that data from any two samples collected under different seasonal or flow conditions could vary from the trend. A seasonal variation in metal content of suspended sediment is supported by the work of Rose (1977) which tentatively identified higher metal content of spoil bank groundwaters during warmer seasons. Further investigation is needed to better identify causes of variations in metal content in the suspended sediment and to

TABLE 4
Mean Metal Content and Range of Mean Metal Content of Suspended Sediment
in Each Stream Over The Study Period
($\mu\text{g/g}$ except Fe)

Sample Site	Mean or Range	Element							
		Co	Cr	Cu	Fe-%	Mn	Ni	Pb	Zn
IF	Mean	48	125	76	20.1	676	114	21	584
	Range	23-94	96-181	36-116	13.1-29.6	453-923	72-161	7-43	148-878
NRaIF	Mean	47	167	142	7.2	760	113	40	388
	Range	16-107	107-204	49-465	3.4-13.4	429-1199	63-267	10-79	199-741
NRbIF	Mean	47	126	109	16.2	600	94	29	447
	Range	15-103	65-209	62-230	5.6-26.7	426-988	35-176	10-48	373-589
BI	Mean	29	116	78	4.7	620	56	34	203
	Range	14-66	51-192	36-84	3.7-7.6	487-764	37-95	13-57	152-294
CB	Mean	38	98	75	5.2	689	40	55	227
	Range	21-69	58-136	70-80	4.7-5.5	636-734	29-45	34-68	187-289

IF-Indian Fork

NRaIF-New River above Indian Fork

NRbIF-New River below Indian Fork

BI-Bill's Branch

CB-Cave Branch

identify effects of stream flow variations on suspended sediment chemistry.

Metal Content of Size Separated Sediment

Size separation, acid digestion, and analysis for metal content on four sets of samples provided data which showed tendencies for specific elements to concentrate in coarse or fine sediment. The suspended sediment load in Bill's Branch, Indian Fork, and New River below Indian Fork was generally high enough to give a useable sample volume in each size fraction after separation of sediment from an 80 liter water sample. Suspended sediment yield in New River above Indian Fork was often insufficient to give useable samples after separation and Cave Branch never produced sufficient sediment to perform separations.

Table 5 presents data from metals analyses of each size fraction for a representative sample from each sample site. Additional data for analyses of size separated samples are given in the Appendix. Figure 5 is a graphic presentation of the metal content in each size fraction of sediment from each stream (data from Table 5). A general increase in metal content was seen in the finer size fractions except for Mn which was typically concentrated in coarser sediment or showed a bimodal distribution in coarse and fine fractions. Factors which favor higher metal content in finer size fractions are: (1) affinity of some metal ions for hydrous Fe oxides, (2) higher ion exchange capacities of fine clay minerals, especially vermiculite and mixed layer minerals, (3) more surface sorption of ions on fine particles with high specific surface areas. Mn occurs as concretionary particles in the coarser sediment and as amorphous coatings in finer fractions. Robinson (1929) explained the

TABLE 5
Metal Content of Size Separated Samples
Collected 4/2/76
($\mu\text{g/g}$ except Fe)

Sample Site	Size Fraction	Element							
		Co	Cr	Cu	Fe-%	Mn	Ni	Pb	Zn
IF	μm								
	>20	17	80	80	10.9	437	23	13	127
	5-20	20	86	78	11.4	434	70	7	78
	2-5	27	110	98	13.7	489	97	24	203
	0.2-2	35	120	210	16.8	376	90	48	301
NRaIF	>20	11	82	15	3.9	720	48	19	-
	5-20	19	320	60	6.4	700	105	27	200
	2-5	16	194	88	7.3	637	53	30	176
	0.2-2	26	222	83	9.4	520	138	51	972
NRbIF	>20	8	91	38	6.5	424	55	14	138
	5-20	10	131	55	12.7	503	79	14	429
	2-5	12	139	95	15.2	430	90	11	550
	0.2-2	32	-	85	20.1	457	48	25	853
Bi	>20	14	52	52	5.7	642	26	18	-
	5-20	12	52	52	6.1	457	42	9	-
	2-5	16	86	92	10.5	472	75	19	107
	0.2-2	Sample lost							

IF-Indian Fork

NRaIF-New River above Indian Fork

NRbIF-New River below Indian Fork

Bi-Bill's Branch

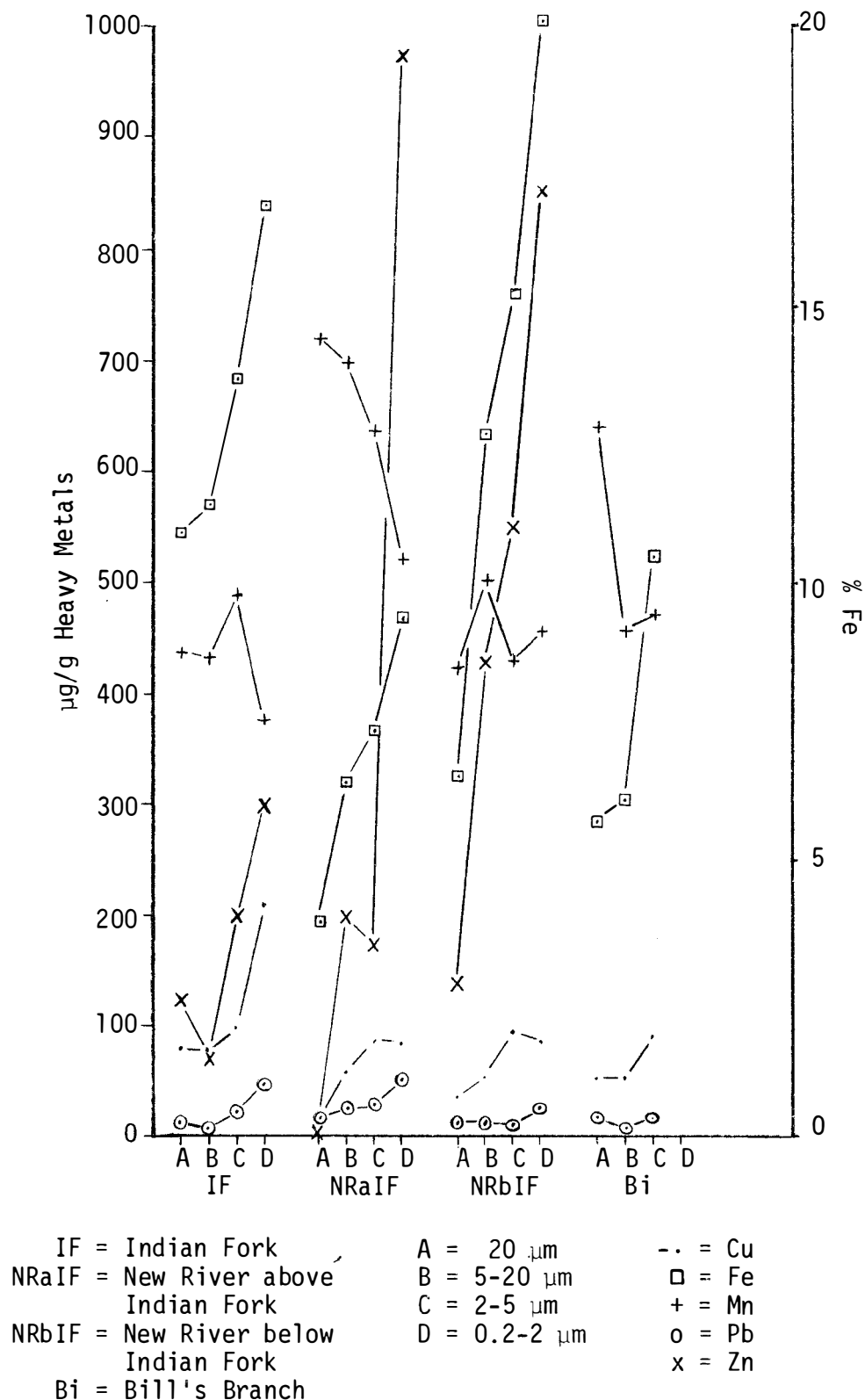


Figure 5. Metal content of each size fraction of suspended sediment from four streams (4/2/76).

accumulation of Mn in coarser particles as a preferential precipitation of Mn from solution on a previously formed Mn rich particle instead of nucleation of new particles.

Extractable Fe-Mn Oxide Content of Suspended Sediment

In order to determine the weight percent of extractable Fe-Mn oxides in the suspended sediment dried sediment samples were weighed before and after extraction of Fe-Mn oxides in a buffered citrate-dithionite solution. Histograms showing the weight percent extractable Fe-Mn oxides in bulk samples from each stream are given in Figure 6. Ranking the streams according to weight percent extractable oxides showed: Indian Fork > (New River below Indian Fork) > (New River above Indian Fork) > Cave Branch > Bill's Branch. This was the same ranking observed in total Fe content of bulk samples from the streams. The fact that Cave Branch had higher oxide content than Bill's Branch was unexpected from knowledge of the surface disturbances in the two watersheds. Possible causes of this are (1) precipitation of Fe and Mn from groundwaters on the available suspended particles, which are less abundant in Cave Branch than in Bill's Branch, resulting in higher extractable oxide levels in the sediment, (2) presence of abandoned deep mines which were not indicated on the Mineral Resources Map (Luther and Avery, 1970) and were not evident in aerial photographs of the watershed. Another possibility is that Fe content in Bill's Branch may increase in the future as groundwaters leach the relatively fresh spoil banks and carry dissolved Fe into the stream.

Weight percent extractable oxides of size separated samples from

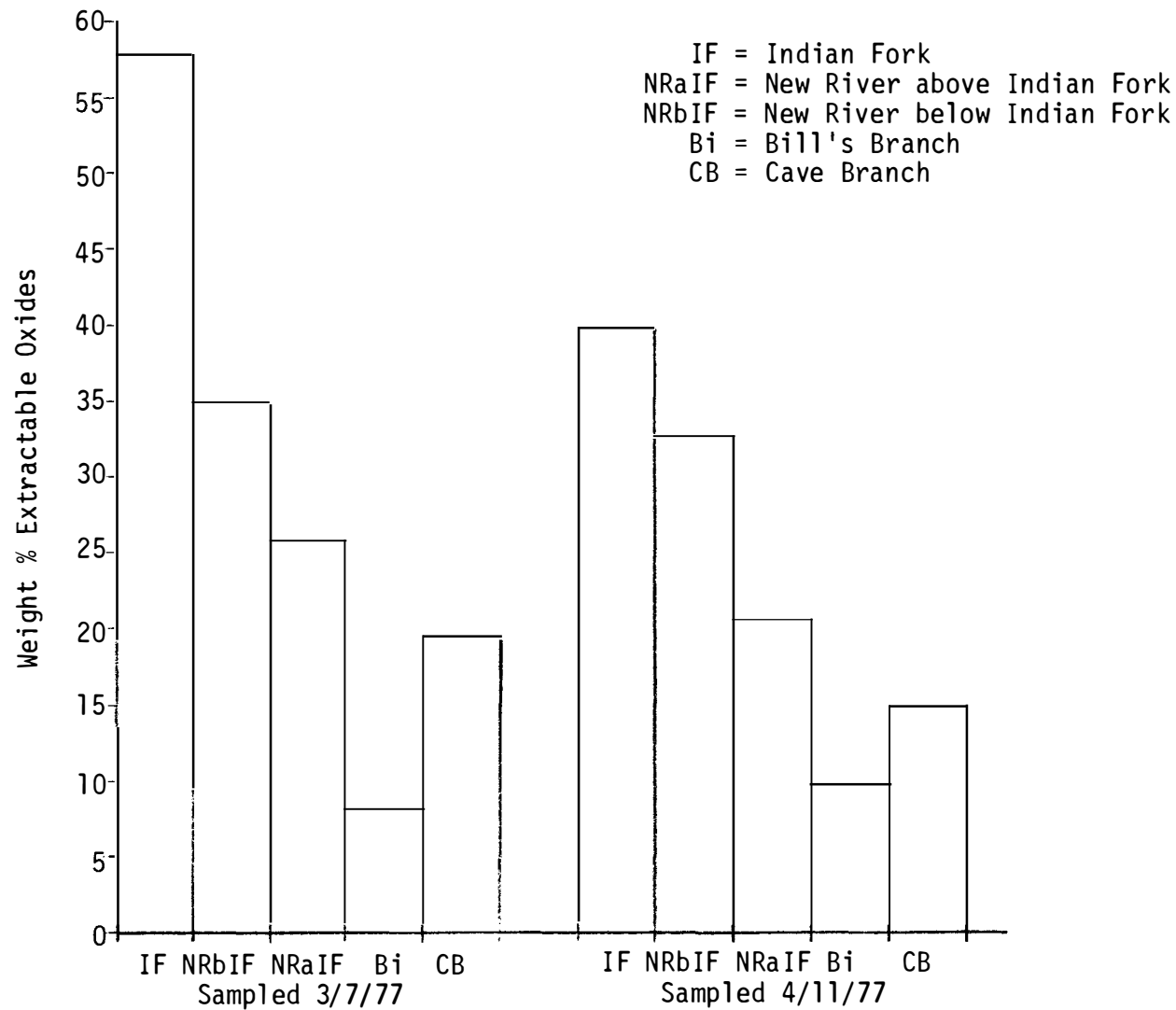


Figure 6. Extractable oxide content of bulk samples from five sample sites.

Indian Fork, New River below Indian Fork, and Bill's Branch were determined and the data were plotted as histogram (Figure 7). The finer size fractions in Indian Fork contained more than 90% extractable oxides. The highest extractable oxide levels occurred in the finer particle sizes in each stream which correlates with Fe content of acid digested samples. The physical importance of the hydrous oxides is apparent in that they comprise a significant volume of the suspended load.

Association of Heavy Metals with Fe-Mn Oxides

The chemical importance of the oxides as a scavenger of heavy metals was determined by chemical extraction of the oxides and analysis of the extract solution. Extraction of hydrous Fe-Mn oxides was readily accomplished using the reducing agent dithionite in a solution containing sodium citrate which chelates ions in solution (Jackson 1956, Jenne et al. 1974). The resulting extract solution had an extremely high concentration of sodium salts and direct analysis by atomic absorption was hampered by clogging of the burner head by the salts. Jenne (1974) proposed an APDC-MIBK concentration of the metals from the extract solution to alleviate this analytical problem. This procedure was attempted on two sets of samples and yielded poor results. Problems encountered were: (1) standards made in a citrate-dithionite solution and extracted into the organic produced a very nonlinear standard curve, 2) though purified reagents were used in all procedures blank values were high, especially for Zn and Cu. The dithionite extraction of Fe and Mn oxides from clays was very effective as a preparatory step for X-ray diffraction studies but was a poor method for trace metal analysis

IF = Indian Fork
NRbIF = New River below Indian Fork
Bi = Bill's Branch

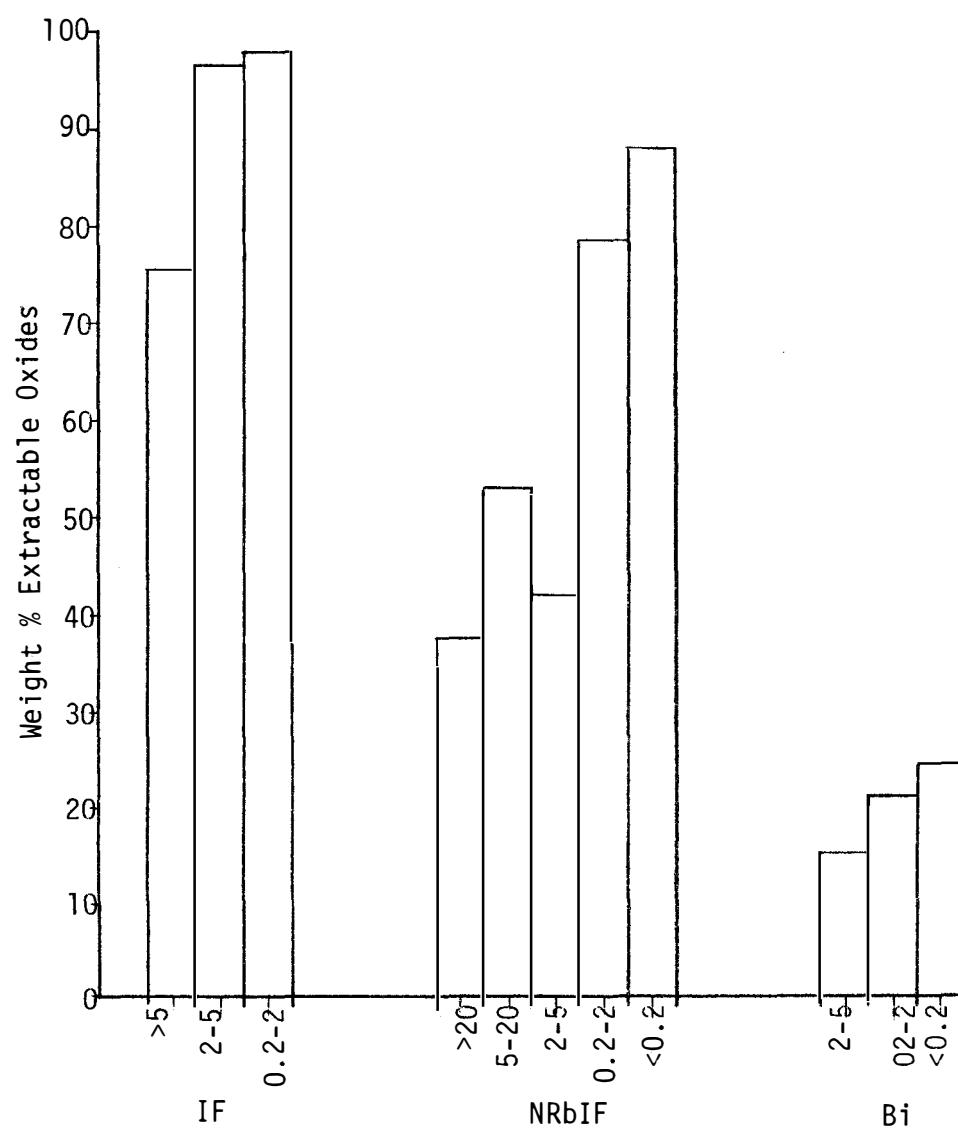


Figure 7. Extractable oxide content of size separated suspended sediment samples from three streams.

because of contamination and analytical problems. Residues from the dithionite extraction were digested and analyzed for Fe and Mn to show the effectiveness of the technique; Fe content of the residue was 1-2% and Mn content was 100-200 $\mu\text{g/g}$.

The 0.3 N HCl extraction method proposed by Malo (1977) was used on unseparated sediment samples from each stream in an attempt to determine which metals tended to accumulate in the acid extractable oxides. Data from analyses of the extract solution and the residue remaining after extraction are shown in Table 6. Comparison of metal content of the extract solution and the residue showed that Co, Cu, and Zn were removed from sediment along with Fe and Mn oxides by the dilute acid treatment. Cr, Ni, and Pb were more evenly distributed between the extractable oxides and the residue.

Residues from the HCl extraction had from about 3% to about 7% Fe while the dithionite extracted residues contained less than 2% Fe. The dilute acid extraction was less effective for total removal of Fe from the sediment than the dithionite method. Mn content of the residues from both extraction methods were similar indicating comparable efficiency of extraction of Mn by both methods. The highest levels of extractable Mn and other metals appeared in Bill's Branch sediment. The work of Massey and Barnhisel (1972) showed rapid solubilization of Mn in early stages of weathering of spoil material with increasing solubilization of Cu, Ni, and Zn until the maximum acidity was reached. High Mn content in the suspended sediment in Bill's Branch may indicate that higher metal content of the sediment will be seen in the future with continued weathering of the still fresh spoil. Mn oxides typically

TABLE 6

Results of Fe Extraction and Residue Analyses
($\mu\text{g/g}$ except Fe)

Sample Site	<u>Metal Content of Material Extracted by 0.3 N HCl</u>								
	Date	Co	Cr	Cu	Fe-%	Mn	Ni	Pb	Zn
IF	3/1/77	33	63	105	36.5	858	79	47	1008
NRaIF	"	81	220	341	18.8	2112	174	174	1157
NRbIF	"	27	63	185	35.2	836	45	113	881
BI	"	186	139	465	19.4	8969	185	278	1022
IF	2/22/77	29	48	92	39.8	884	76	23	1318
NRaIF	"	45	179	268	10.0	768	45	BDL	1160
NRbIF	"	22	40	188	37.2	907	34	49	963
BI	"	88	294	294	17.6	3456	74	117	1029

Sample Site	<u>Metal Content of Residues from 0.3 N HCl Extractions</u>								
	Date	Co	Cr	Cu	Fe-%	Mn	Ni	Pb	Zn
IF	3/1/77	16	198	19	7.0	186	105	23	192
NRaIF	"	7	200	30	4.1	147	118	14	156
NRbIF	"	11	148	32	3.6	178	95	27	192
BI	"	11	45	19	3.2	137	37	26	99
IF	2/22/77	21	239	17	2.4	143	115	48	224
NRaIF	"	BDL	179	27	3.6	89	80	32	321
NRbIF	"	8	90	28	5.2	184	37	46	185
BI	"	33	66	19	2.8	94	31	47	118

IF-Indian Fork
NRaIF-New River above Indian Fork
NRbIF-New River below Indian Fork
BI-Bill's Branch

BDL-Below Detection Limit

have a higher scavenging capacity than Fe oxides and this may be reflected in the high heavy metal values along with the high Mn values in Bill's Branch sediment.

Effect of Mining Activities on Suspended Sediment

Effects of mining on suspended sediment must be evaluated in the perspective of the bedrock and soil systems and the processes acting in and on those systems. The bedrock and soil materials in any stream basin contain a fixed volume of metals and minerals. These materials will eventually move through the fluvial system in some form by natural weathering and erosion processes. Coal extraction and the associated disturbance of soil and bedrock affect two parameters of the weathering and transport system: (1) availability of sediment to erosion, (2) rate of mobilization of metals by chemical weathering of bedrock materials containing high levels of metals by exposure of the materials to air and water. Mining activities expose large volumes of bedrock to weathering conditions and the more abundant and more mobile elements (Fe, Mn, and Zn as determined in this study) are carried into surface waters where they are found in elevated levels in suspended sediment especially as oxide coatings and floc.

The effects of mining on the suspended sediment and use of suspended sediment as a measure of mining impact must be evaluated on the following bases:

- (1) total suspended sediment load carried out of a watershed
over a period of time
- (2) metal content of the sediment

- (3) composition of the sediment in terms of mineralogy and Fe-Mn oxide content.

A rigorous assessment of the effect of mining on the heavy metal content of suspended sediment requires data on the total suspended load with time; these data are not available for streams in the study area but it was observed that streams in mined watersheds carried heavier sediment loads than streams in unmined watersheds. Chemical data obtained in this study showed that Fe, Mn, and Zn content was higher in suspended sediment in extensively mined watersheds than in sediment in unmined watersheds. Elevated levels of some metals and average levels of others in suspended sediment in mined watersheds coupled with higher suspended load in these watersheds indicate that a higher total volume of metals is carried through the fluvial system in suspended sediment in mined watersheds than in unmined watersheds. The effect is an accelerated rate of movement of the metals which is related to mining activities. Assumptions that surface mines were the source of these metals as opposed to abandoned auger mines or deep mines can be neither supported nor refuted by data obtained in this study.

The effects of mining activities on the mineral content of suspended matter were found to be:

- (1) an increase in the Fe-Mn oxide content of the sediment
- (2) erosion of less thoroughly weathered clay minerals and consequently more chlorite and less vermiculite in the suspended sediment of streams in mined watersheds.

The high Fe-Mn oxide content which results from mining is significant as a chemical sink for Zn, Co, and Cu and physically as a volumetric

component and as a particle cementing or binding agent. The chlorite and vermiculite content of the sediment is probably less significant than the high Fe-Mn oxide levels in mined watersheds since the 14⁰ minerals were at most a minor component of the total suspended load.

Conclusions

Investigation of metal content of suspended sediment showed:

- (1) Fe content of suspended sediment showed a consistent pattern in the streams sampled; high Fe content was coincident with severe disturbance by mining activity in small watersheds.
- (2) Zn showed an association with Fe content in the suspended sediment.
- (3) Fe, Mn, and Zn content of suspended sediment in disturbed watersheds was higher than that of clay size bottom sediment in Lowe Branch, the undisturbed control stream. Values for other metals in the suspended sediment were similar to or lower than values for bedrock or the clay size fractions of bottom sediment in Lowe Branch.
- (4) Metal content of suspended sediment increased in the finer size fractions.
- (5) Hydrous Fe-Mn oxides were found to be important as a physical component of the sediment as 50% by weight of Indian Fork was dithionite extractable Fe-Mn oxides. Co, Cu, and Zn were extracted from sediment along with Fe and Mn.
- (6) Little correlation was found between severity of surface disturbance and heavy metal content of suspended sediment (except the Fe, Mn and Zn contents previously mentioned). Suspended load of streams in heavily disturbed watersheds was higher than in lightly disturbed or

undisturbed watersheds. An assessment of the total suspended load carried by each stream over a long period of time and calculation of the total volume of heavy metals carried in the suspended matter would provide a realistic measure of the effects of mining on the metal content of the sediment.

V. SUMMARY

Suspended sediment is important as a medium of transport of mineral material in the fluvial system as well as being an important control on water chemistry. Suspended sediment characteristics which were studied in this investigation included size distribution, mineralogy, total heavy metal content as a function of watershed disturbance, heavy metal distribution as a function of particle size, and the effects of hydrous Fe-Mn oxides on the distribution of minerals between different size fractions and on heavy metal distribution.

Suspended sediment size distribution histograms prepared for four streams with varying types of surface disturbance showed no significant systematic variations in sediment distribution. The 2-5 μ m class was the modal class in all samples which were size separated by continuous flow centrifugation. Variation in stream flow varied the total load in suspension without producing significant shifts in the distribution histograms. Extraction of hydrous Fe-Mn oxides and separation of clay residues for X-ray study indicated that oxide coatings increased the size of individual particles and were significant in cementation of flocculated particles. Suspended sediment load in severely disturbed watersheds was significantly higher than in undisturbed or lightly disturbed watersheds as a result of higher erosion rates and formation of hydrous oxide floc.

A bulk mineralogical analysis of suspended sediment from streams with different degrees of disturbance showed that the dominant minerals

in suspension in all streams in the area were quartz, kaolinite, and illite. Chlorite, vermiculite, lepidocrocite, and mixed layer clays were present as minor components of the sediment. Chlorite predominated over vermiculite in areas where surface disturbance exposed bedrock to rapid weathering in spoil banks but vermiculite predominated over chlorite where soils were the source of clay to the streams.

Hydrous Fe-Mn oxides which are largely amorphous (and therefore are not minerals) were important physical and chemical components of the suspended sediment in mined areas as they were present in excess of 50 weight percent of the total suspended load in Indian Fork. Highest oxide content was found in a watershed with extensive disturbance of soil and bedrock by mining. Flocculation of clays and cementing by hydrous oxides obscured the tendency for kaolinite to concentrate in coarser clay size particles.

Comparison of heavy metal content of suspended sediment in disturbed watersheds with background levels in bedrock and with clay size bottom sediment in an undisturbed stream showed that Fe, Mn, and Zn were significantly enriched in the suspended sediment. Fe, Mn, and Zn were present in the bedrock in higher concentrations than most of the other heavy metals and they are more mobile in slightly acid environments and thus were readily leached from spoil and bedrock materials and precipitated in the oxidizing conditions of surface streams. Other metals such as Cr, Ni, Pb, and Co were present in suspended sediment in about the same or lower concentrations as in bedrock and in lower concentrations than in clay fractions of bottom sediment in an undisturbed watershed. Surface and bedrock disturbance permits rapid weathering of shales and

mudstones which erode rapidly and contribute clays to the suspended load and in effect may dilute the sediment with low metal material. Cu and Pb showed enrichment in suspended sediment in summer samples when low flow conditions prevailed.

Total heavy metal content was generally highest in the finer size fractions; increases in Fe, Zn, Cu, Co, Cr, and Ni were seen in finer size fractions of size separated samples. Cr often showed high values in coarse and fine fractions with lowest values in the coarse clay. Mn content typically was high in the coarse size fractions but sometimes showed a bimodal distribution with maxima in coarse and fine fractions. An association of Fe and Zn content was detected in samples from different streams and within size separated samples from a single stream. Dilute acid extraction of sediment samples showed that high levels of Cu, Fe, Mn, and Zn were present in extractable forms and that Co, Cr, Ni, and Pb were more evenly distributed between readily extractable materials (hydrrous oxides and organic complexes) and residue materials. The 0.3 N HCl extraction was an extreme method compared to a dithionite extraction at neutral pH and was used after citrate-dithionite extraction proved unsatisfactory for trace metal analysis in these samples. Acid extraction not only reduces and dissolves hydrous Fe-Mn oxides but can destroy metalorganic complexes and remove ions from exchange sites in clay minerals. Malo (1977) compared the acid extraction with several other partial extraction methods and found metal values of the 0.3 N HCl method comparable to those of a pH 3 citrate-dithionite extraction. The acid extraction as used here did not clearly indicate metal associations with

oxide fractions of the sediment but it did indicate metals content which was present in a reactive state and which might be expected to react in acid and reducing conditions in the stream environment.

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APPENDIX

SEDIMENT SIZE SEPARATION PROCEDURE

- (1) Centrifuge by continuous flow at maximum velocity (20,000 rpm, 300 ml/min) to consolidate sediment out of the 80 liter water sample. A Sorvall RC2-B superspeed centrifuge equipped with an SS-34 rotor and continuous flow apparatus were used.
- (2) Resuspend the sediment and use gravity settling in a 1 liter tall form beaker to remove all sediment $<5\mu\text{m}$. Settling time for this step is 1 hour 15 minutes for particles $>5\mu\text{m}$ diameter to settle 10 cm. @20 °C.
- (3) Separate 5-20 m and 20 m particles by settling for 4 minutes and 40 seconds before decanting.
- (4) Clay fractions are separated by continuous flow centrifugation. Separate the 2-5 m particles from 0.2 m particles by continuous flow using rotor speed of 5000 RPM and flow rate of 275 ml/min. Resuspend the 2-5 m sediment and re-centrifuge at least 3 times.
- (5) Remove the 0.2-2 m particles by continuous flow centrifugation at 10,000 RPM and flow rate of 300 ml/min. Resuspend and re-centrifuge at least 3 times.
- (6) Remove sediment 0.2 m diameter by centrifuging supernatant from 0.2-2 m separation at 20,000 RPM and flow rate 300 ml/min. This should remove particles down to about 0.02 μm diameter.
- (7) Place all samples in low temperature oven (40°C) to dry in Pyrex beakers.

ACID DIGESTION PROCEDURE

Reagents:

Concentrated HNO_3
" HF
" HClO_4
1 N HCl

- (1) Dried samples (0.1000-0.3000g) is weighed into preweighed teflon beaker.
- (2) Add 5ml concentrated HNO_3 to sample, place in sandbath and heat at 130°C to dryness.
- (3) Add 5ml HF and 1ml HClO_4 and heat at $225-240^\circ\text{C}$ with beaker completely covered until all particles are digested. This may require addition of more HF . When all sediment is digested cover may be partially removed to speed evaporation. Acid must be evaporated to dryness in this step.
- (4) Add 5ml of 1 N HCl and boil with cover on for several minutes to dissolve all salts. Add a few ml deionized water rinsing beaker walls, remove from heat.
- (5) Bring to 25ml volume in a volumetric flask using deionized water as the dilutant. Transfer to Nalgene bottle for storage and analysis.

CITRATE-DITHIONITE EXTRACTION OF HYDROUS Fe-Mn OXIDES

- (1) Weigh sample (not more than 0.300 g) into centrifuge tube with cap.
- (2) Add 25 ml of freshly prepared citrate-dithionite solution.
The solution is: 0.2 M with respect to citric acid monohydrate
0.3 M with respect to Na citrate
0.3 M with respect to $\text{Na}_2\text{S}_2\text{O}_4$ (dithionite)
- (3) Place capped centrifuge tubes on wrist action shaker and agitate for 30 minutes.
- (4) Place centrifuge tubes in centrifuge and spin down the sediment.
- (5) Decant the supernatant into bottles for Fe-Mn analysis.
- (6) Repeat steps 2-5.
- (7) Wash the sediment by suspension in deionized water and spin down on the centrifuge. Discard the wash water. Repeat the wash 3 times.
- (8) Dry the sediment in centrifuge tubes in low temperature (40°C) oven. Re-weigh tubes with dry sediment to determine weight percent of sample extracted.

TABLE 7
Sediment Size Distribution Data
All Values Are Percentages

Sample Site	Size Fraction	Sample Dates and Sediment Distribution Data											
	um	2/16/76	4/2/76	6/29/76	7/12/76	9/28/76	11/22	1/23/77	2/11/77	2/12/77	2/14/77	2/15/77	2/21/77
IF	20	-	19.8	9.5	6.1	12.8				5.8			
	5-20	27.4	36.3	1.3	12.0	-	12.0			9.5			
	2-5	71.4	38.6	69.6	52.6	81.5	43.3			57.6			
	0.2-2	1.3	5.2	14.3	25.8	5.6	44.6			25.8			
	0.2	-	-	5.0	3.4	-	-			1.1			
NRaIF	20	-	40.9	Not Separated	11.2	-			19.2				
	5-20	37.7	30.6		14.4	6.3			4.4				
	2-5	62.3	17.3		74.4	67.5			48.6				
	0.2-2	-	11.0		-	26.0			26.1				
	0.2	-	-		-	0.1			1.6				
NRbIF	20	-	31.5	-	7.5	2.7		2.2			6.5		
	5-20	69.5	36.2	8.9	13.5	4.5		18.3			12.8		
	2-5	25.9	28.2	81.4	62.0	55.0		39.8			56.5		
	0.2-2	4.5	3.9	9.6	16.8	30.8		18.1			16.1		
	0.2	-	-	-	-	0.9		23.5			7.9		
BI	20	-	17.6	No Sample	7.3	7.2					7.3		-
	5-20	62.6	29.2		1.3	9.2					13.3		-
	2-5	23.5	28.5		68.5	64.3					46.2		48.4
	0.2-2	13.9	24.6		13.3	19.2					29.2		31.5
	0.2	-	-		9.3	-					24.5		20.1

IF-Indian Fork

NRaIF-New River above Indian Fork

NRbIF-New River below Indian Fork

BI-Bill's Branch

(-)-Insufficient Sample

TABLE 8
Metal Content of Sediment
(6/29/76 and 7/12/76)

Sample Site	Size Fraction	Co	Cr	6/29/76		Fe-%	Mn	Ni	Pb	Zn
				Cu						
	μm									
IF	>20	67	88	36	5.8	908	81	17	225	
	5-20	130	222	131	22.9	916	131	30	589	
	2-5	103	84	68	19.0	988	151	12	632	
	0.2-2	90	125	82	22.4	721	165	13	656	
	<0.2	115	211	72	23.1	1003	193	13	752	
NRaIF	Bulk	102	203	192	10.8	1199	90	10	600	
NRbIF	5-20	64	212	94	13.6	723	BDL	17	340	
	2-5	80	75	133	22.1	455	126	12	451	
	0.2-2	96	199	263	23.0	287	64	15	557	
<u>7/12/76</u>										
IF	5-20	89	192	89	17.7	1147	130	14	261	
	2-5	99	119	93	29.2	1001	167	7	608	
	0.2-2	85	143	146	34.7	740	175	3	631	
	<0.2	91	428	146	43.3	574	73	5	593	
NRaIF	>20	-	-	189	8.3	943	283	66?	478	
	5-20	-	-	221	7.3	1470	92	37	536	
	2-5	107	-	556	15.4	1068	299	33	1140	
NRbIF	5-20	71	357	171	16.8	1093	71	24	464	
	2-5	96	156	227	27.2	630	199	11	675	
	0.2-2	86	286	286	34.8	532	137	18	371	
BI	>20	-	60	20	2.2	697	50	20	-	
	5-20	-	-	-	2.6	556	55	BDL	-	
	2-5	64	188	64	4.6	701	95	13	193	
	0.2-2	74	230	110	5.5	548	110	25	197	
	<0.2	71	299	110	6.4	472	118	25	189	

IF-Indian Fork

NRaIF-New River above Indian Fork

NRbIF-New River below Indian Fork

BI-Bill's Branch

BDL-Below Detection Limit

(-)-Insufficient Sample For Analysis

TABLE 9
Metal Content of Sediment
(9/28/76)

Sample Site	Size Fraction	Co	Cr	9/28/76 Cu	Fe-%	Mn	Ni	Pb	Zn
	μm								
IF	>20	34	144	67	8.1	749	-	-	326
	5-20	Insufficient Sample							
	2-5	37	101	118	16.2	364	-	43	576
	0.2-2	38	198	193	15.8	330	-	39	1322
NRaIF	>20	Sample Lost in Processing							
	5-20	51	128	112	1.1	1371	146	-	277
	2-5	41	116	83	3.9	731	113	37	281
	0.2-2	36	102	84	3.4	527	106	38	246
	<0.2	Sample Lost in Processing							
NRbIF	>20	111	161	-	4.3	1485	-	16	136
	5-20	Insufficient Sample							
	2-5	94	128	78	4.7	1027	138	7	258
	0.2-2	111	124	129	6.3	943	192	11	381
	<0.2	110	126	147	7.1	882	186	13	471
BI	>20	-	182	51	4.0	1063	111	-	233
	5-20	-	145	40	4.6	933	105	-	289
	2-5	23	108	85	4.2	762	65	-	229
	0.2-2	31	357	115	4.6	576	99	-	538

IF-Indian Fork

NRaIF-New River above Indian Fork

NRbIF-New River below Indian Fork

BI-Bill's Branch

(-)-Insufficient Sample For Analysis

X-RAY DIFFRACTION DATA

X-ray diffraction data are presented here in reduced diffraction patterns and in tabular form. The diffraction patterns show that the major peaks are at $14\text{\AA}$, $10\text{\AA}$, $7\text{\AA}$, $5\text{\AA}$, and $4.26\text{\AA}$. The $10\text{-}14\text{\AA}$ "intergrade" material is apparent in the patterns as a series of peaks or as a saddle between the $10\text{\AA}$ and $14\text{\AA}$ peaks. Heat treatment of sediment samples generally destroyed most of the intergrade material and reduced the intensity of the $14\text{\AA}$ peak: this decrease in intensity of the $14\text{\AA}$ peak was interpreted as dehydration of vermiculite. Glycolation produced a very weak peak near $17\text{\AA}$ which was caused by expansion of smectite minerals. The $17\text{\AA}$ peak was always weak and was not detected in all samples. Mixed layer clays are indicated by spikes on the background curve between 2° and $5^\circ 2\theta$. Diffraction patterns from a sample of dark shale shows that the mineral composition of the shale is about the same as that of the sediment; the major difference being intensification of the $14\text{\AA}$ peak with heat treatment. This is interpreted as dehydration of a partially weathered or slightly hydrated chlorite.

Data presented in tabular form show the d-spacing of observed peaks and the intensity of those peaks as measured above the background level. Data are presented for untreated samples and glycolated samples from Indian Fork, Bill's Branch, and New River below Indian Fork. Data obtained from Fe extracted samples from Indian Fork and New River below Indian Fork are also presented.

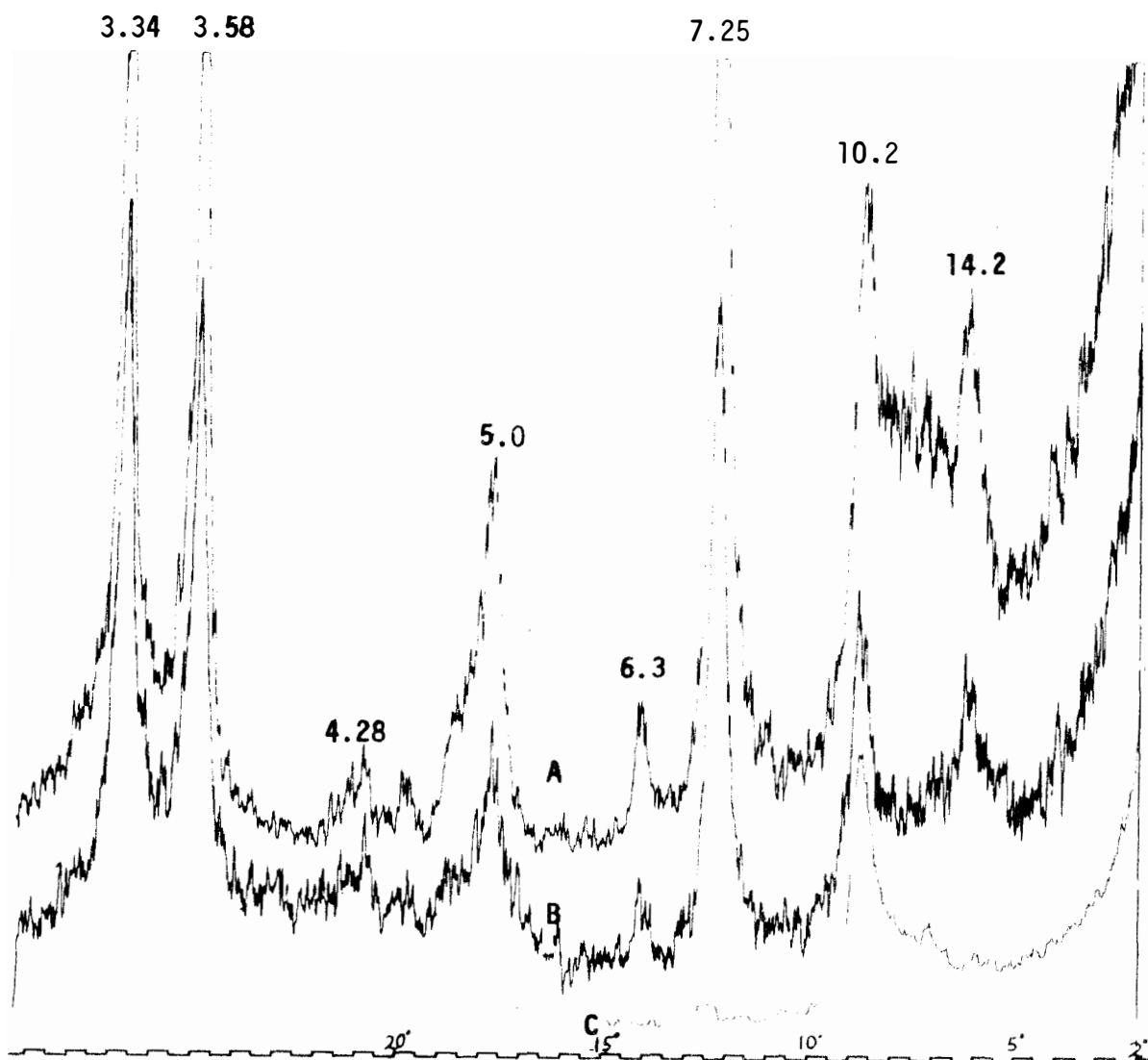


Figure 8. X-ray diffraction patterns from 0.2-2 μm sediment from Bill's Branch. A = untreated; B = glycolated; C = heat treated. Peak values are d-spacing in Å.

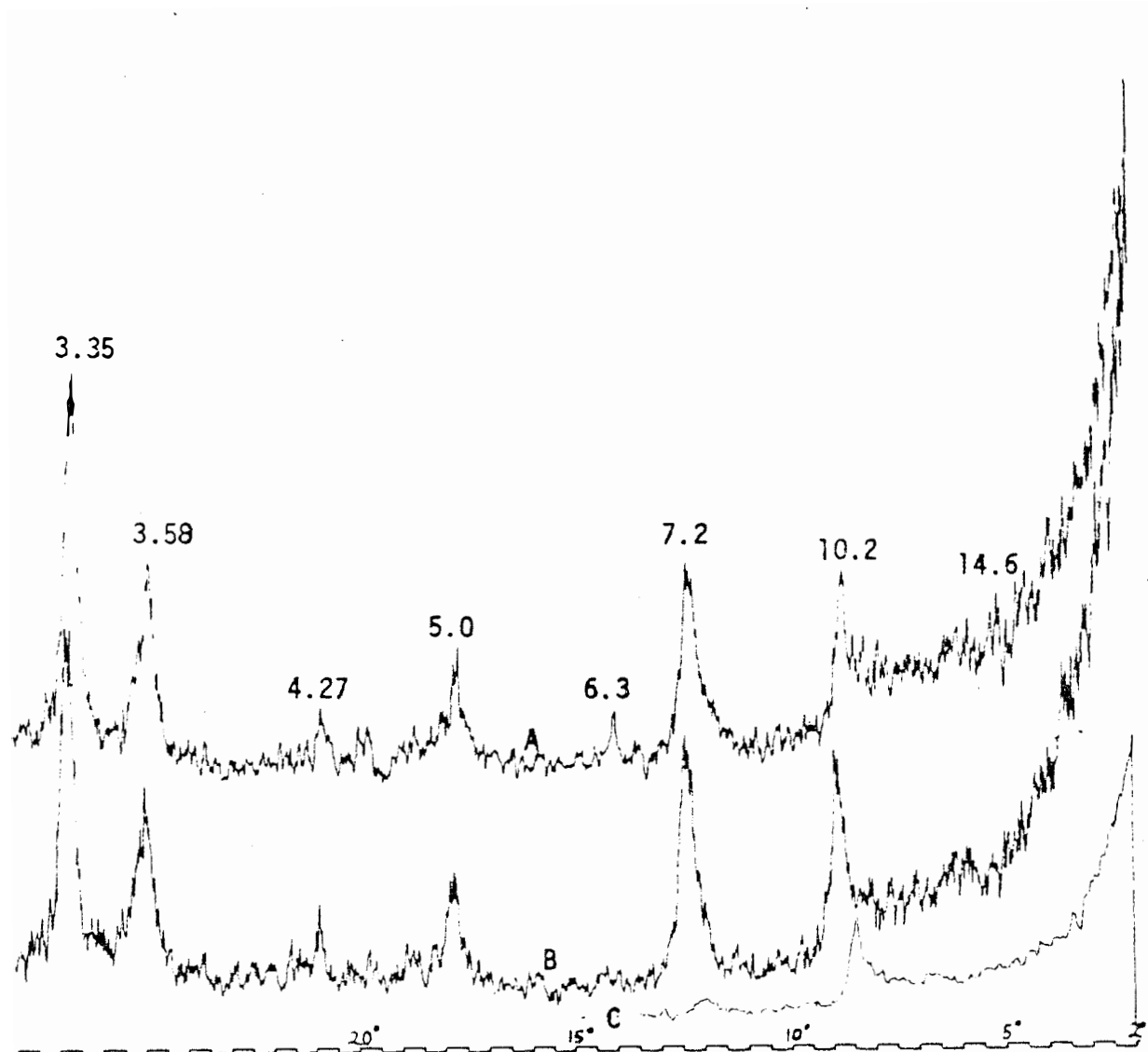


Figure 9. X-ray diffraction patterns from 0.2-2 μm sediment from Indian Fork. A = untreated; B = glycolated; C = heat treated. Peak Values are d-spacing in A.

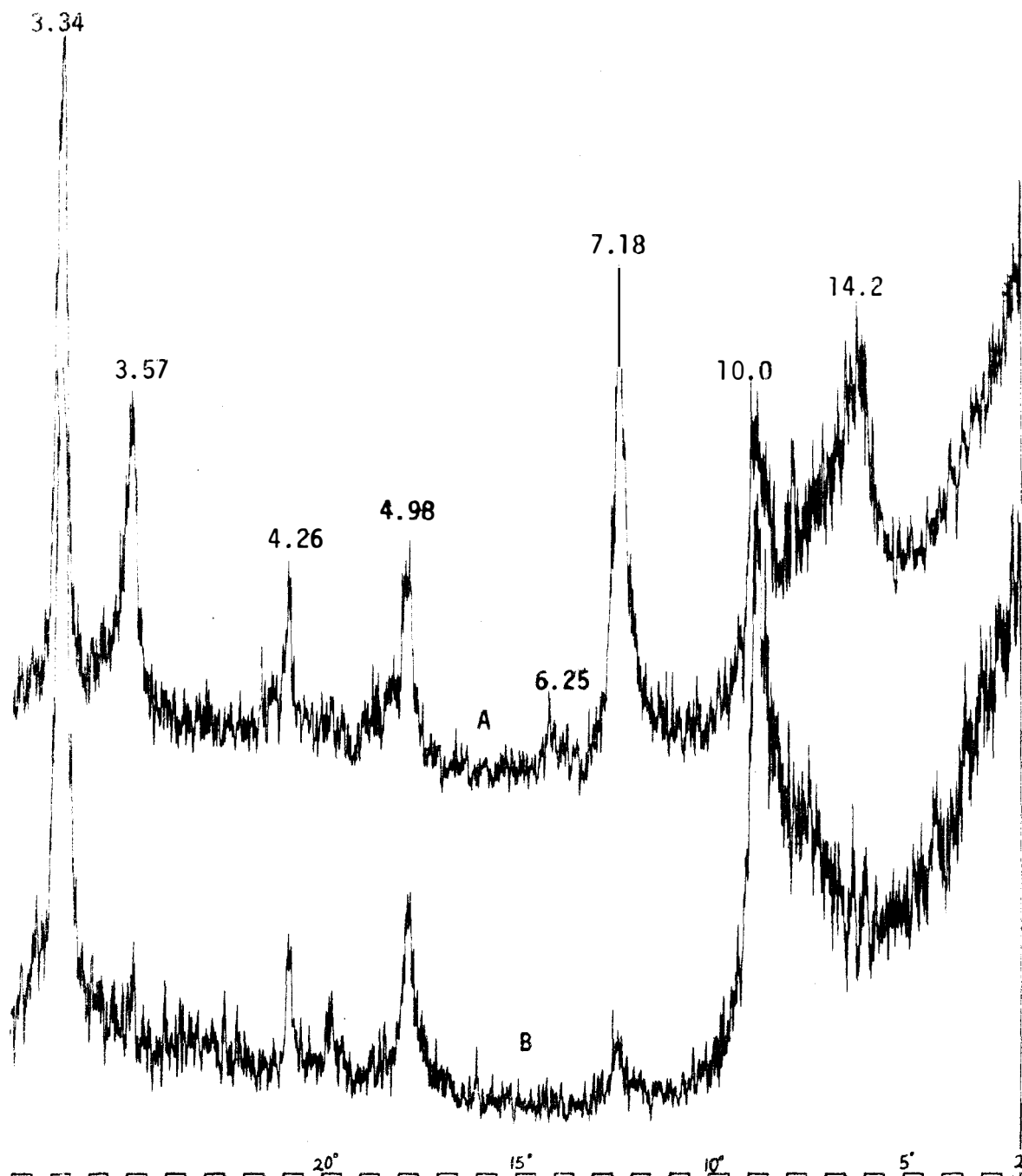


Figure 10. X-ray diffraction patterns from Cave Branch sediment. A = untreated; B = heat treated. Peak values are d-spacing in Å.

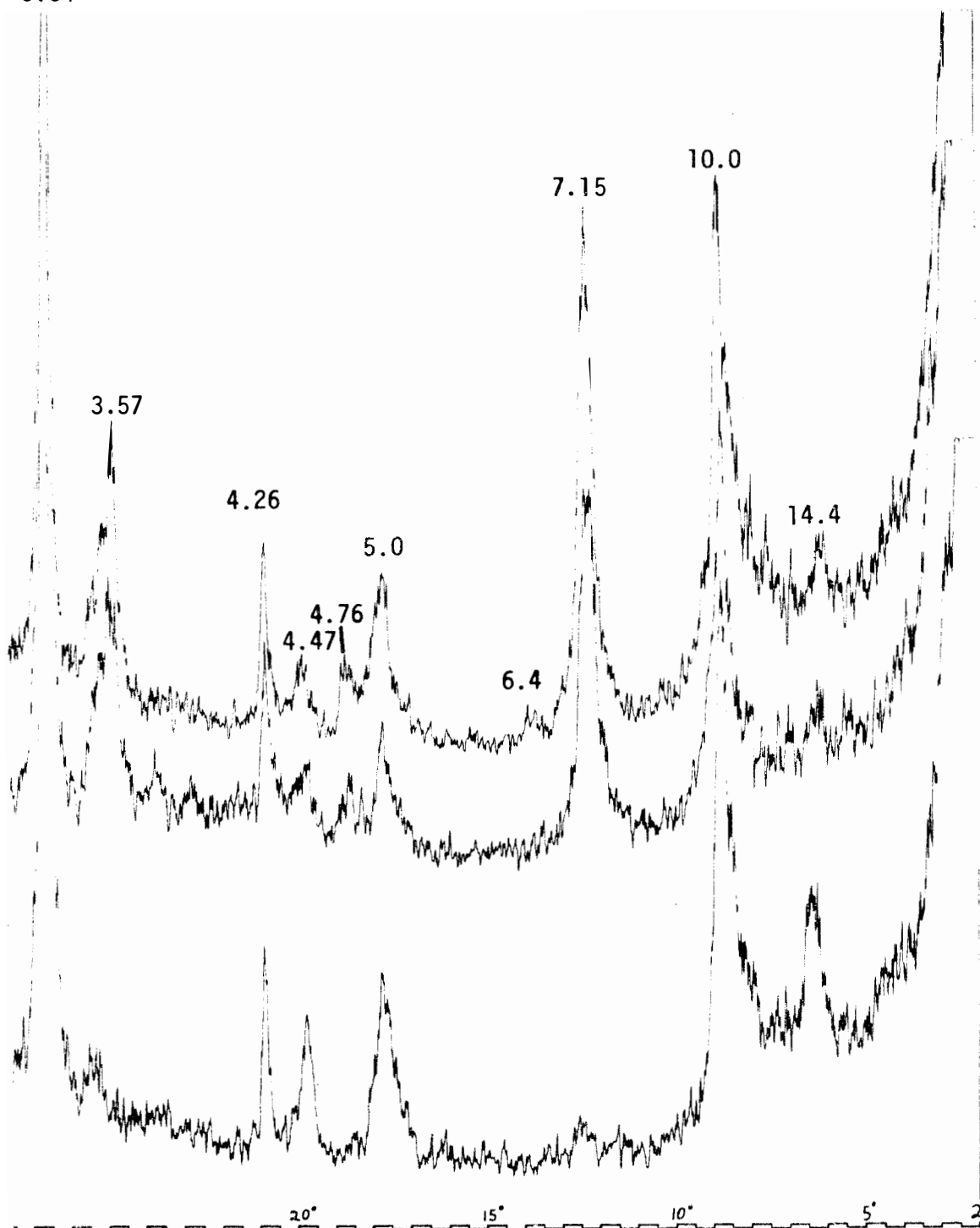


Figure 11. X-ray diffraction patterns from a dark shale sample.
A = untreated; B = glycolated; C = heat treated.
Peak values are d-spacing in Å.

TABLE 10
Diffraction Data from Indian Fork Samples
Scale 100

Untreated		Glycolated		Untreated		Glycolated	
d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I
<0.2 μ m				0.2-2 μ m			
14.5	7	13.8	8	22.6	5		
10.1	21	10.1	22	14.6	5	14.2	6
7.2	28	7.2	32	11.2	8	11.5	6
5.2	10	4.99	12	10.2	18	10.1	23
4.5	3	4.5	4	7.2	22	7.15	28
4.27	3	4.27	5	6.3	6	6.28	3
				5.05	14	4.95	12
				4.5	3	4.5	3
				4.27	6	4.25	8
2-5 μ m				5-20 μ m			
14.4	10	14.3	9	13.7	4	14.2	5
12.4	9	12.3	7	10.2	13	10.2	15
10.2	30	10.1	31	7.2	18	7.2	15
7.2	32	7.2	39	6.3	3	6.3	4
5.0	18	5.0	18	5.0	7	5.0	6
4.7	5	4.7	6	4.47	4	4.5	4
4.5	3	4.5	4	4.28	8	4.27	5
4.28	14	4.26	12				

I = Peak Intensity

TABLE 11

Diffraction Data from Fe Extracted
Samples from Indian Fork
(Scale 200)

Untreated		Glycolated		Untreated		Glycolated	
d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I
0.2-2 μ m				2-5 μ m			
14.5	4	14.2	6	14.1	19	14.0	15
10.1	25	10.1	19	10.0	69	10.1	39
7.18	34	7.2	28	7.19	86	7.18	72
5.0	18	4.98	12	4.98	35	4.98	17
4.7	12	4.7	9	4.7	9	4.7	7
4.5	3	4.46	5	4.5	3	4.5	2
4.27	11	4.25	8	4.25	12	4.25	9

I = Peak Intensity

TABLE 12

Diffraction Data from Bill's Branch Samples
(Scale 100)

Untreated		Glycolated		Untreated		Glycolated	
d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I
0.2 μ m				0.2-2 μ m			
19.2 ?				21.5	8	22	10
		17	4	14.2	40	14.5	24
14.2	36	14.3	16	10.0	65	10.1	38
10.3	45	10.1	24	7.2	>100	6.25	10
6.25	12	6.25	6	5.05	47	5.05	25
5.05	30	4.98	21	4.49	8	4.50	8
4.49	7	4.50	5	4.26	10	4.28	12
4.28	4	4.25	3				
2-5 μ m							
		23.6	5				
14.7	34	17.1	20				
10.2	64	10.0	56				
7.25	100	7.15	66				
6.3	8	6.27	4				
5.04	36	4.95	24				
4.51	6	4.50	4				
4.28	12	4.25	14				

I = Peak Intensity

TABLE 13

Diffraction Data for Samples from
New River below Indian Fork
(Scale 100)

Untreated		Glycolated		Untreated		Glycolated	
d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I
0.2-2 μ m				2-5 μ m			
17.8	4	17.3	4	17.3	5	17.4	5
14.2	5	14.2	8	14.6	6	14.5	8
10.2	22	10.0	25	11.1	4	11.0	6
8.9	3			10.0	22	10.1	28
7.21	20	7.15	27	6.3	5	6.3	4
6.4	2	6.4	4	5.01	13	5.0	9
5.05	11	5.04	8	4.73	4		
4.75	4	4.70	5	4.52	3		
4.50	5	4.50	6	4.27	13	4.26	10
4.28	11	4.25	9				
5-20 μ m							
19.2	4	18.8	2				
14.2	4	14.2	5				
12.2	3	12.2	2				
10.0	21	9.9	20				
7.15	16	7.15	16				
6.3	2	6.4	2				
4.97	8	4.97	11				
4.75	3	4.70	4				
4.47	4	4.45	7				
4.25	19	4.24	20				

I = Peak Intensity

TABLE 14

Diffraction Data for Fe Extracted Sediment from
New River below Indian Fork
(Scale 200)

<u>Untreated</u>		<u>Glycolated</u>		<u>Untreated</u>		<u>Glycolated</u>	
<u>d (Å)</u>	<u>I</u>	<u>d (Å)</u>	<u>I</u>	<u>d (Å)</u>	<u>I</u>	<u>d (Å)</u>	<u>I</u>
<u>0.2μm</u>				<u>0.2-2μm</u>			
16	11	15.7	7			17.5	5
14.5	7	14.1	5	14.1	7	14.3	7
10.0	14	10.1	10	10.0	32	10.0	30
8.8	4					8.25	3
7.18	23	7.18	17	7.18	53	7.2	45
6.35	4			4.98	20	4.99	20
4.97	10	5.01	7	4.70	7	4.70	5
4.78	11			4.48	4	4.50	5
4.70	18	4.72	15	4.26	13	4.26	12
4.45	5	4.38	7				
4.25	5	4.26	6				
<u>2-5μm</u>							
21.5	3	21.0	4				
14.1	9	14.0	7				
11.8	4	11.7	4				
10.0	38	10.0	39				
7.18	46	7.10	46				
4.98	18	4.97	25				
4.72	6	4.73	7				
4.48	4	4.45	5				
4.25	18	4.25	17				

I = Peak Intensity

VITA

Richard H. Ketelle was born in Oak Ridge, Tennessee on July 13, 1950. He attended the Oak Ridge schools and graduated from high school in 1968. He attended Wilmington College in Wilmington, Ohio from 1968 to 1970. In 1973 he received his B.S. degree in Geology from the University of Tennessee. Following graduation he worked at LeConte Lodge in the Great Smoky Mountains. In 1975 he returned to Graduate School at the University of Tennessee. Graduate studies in geology emphasized mineralogy, sedimentology, and low temperature geochemistry.