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HEAVY METAL ANALYSIS OF STREAM SEDIMENTS IN THE JAMES RIVER BASIN, MISSOURI

by

WILLIAM J. HEAD, 1949-

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CONTENTS

CONTENTS (continued)

APPENDIXES

ILLUSTRATIONS

TABLES

HEAVY METAL ANALYSIS OF STREAM SEDIMENTS IN THE JAMES RIVER BASIN, MISSOURI

William J. Head

ABSTRACT

A reconnaissance survey of stream sediments using the minus 80 mesh sieve fraction was made at 53 sites throughout the James River basin, Missouri. Sample sites within the 1460 square miles of the basin were chosen at tributary confluences, suspected contamination sources, and known areas of mineralization. Replicates and stream profiles were taken to check for analytical variation and reproducibility of results. Sediment samples were prepared by a hot nitric acid leach method. The sediments were analyzed using an atomic absorption unit to determine Cu, Pb, Zn, and Cd trace metal contents.

Values of selected streams within the basin were statistically evaluated using Student's t-test and analysis of variance methods to examine variations in metal content of stream sediments. The results were compared with direct observations of the stream populations and found compatible. High metal values in the fine fraction of the stream sediments were found all along the flow of Wilson Creek, and near mineralized areas on Pearson Creek, Finley Creek, and Flat Creek. Lead ranged from 10 ppm to 570 ppm. Zinc ranged from 5 ppm to 610 ppm. Copper ranged from 0 to 98 ppm. Cadmium ranged from 0 to 62 ppm. Average values for Wilson Creek were found to be much higher than average values for the rest of the river basin.

INTRODUCTION

PURPOSE

The water quality of the Springfield-James River basin, Missouri area has been the center of much interest in the past several years. Frequent fish kills in Wilson Creek-James River, the relationship of surface water to weak base metal sulfide mineralization, recreational value of the river, industrial use of the waters, and possible use as a major source of water by the expanding city of Springfield have generated a need for adequate information on the chemical characteristics of the James River water basin. A project was outlined (Proctor, 1972) to test the heavy metal characteristics of surface waters in the James River Basin. A related investigation of the base metal content of the stream sediments was also initiated to increase our knowledge of the river basin and to determine possible sources of the heavy metals.

SCOPE

Sediment samples were collected at 53 different sites within the James River basin. Seasonal replication was made at approximately 30% of the sample sites. Stream sediment sample profiles were also taken across the channel at six sites: These included profiles on the James River, Pearson Creek, Finley Creek, and two on Wilson Creek. These channel profiles consisted of a bank and stream sample on each side of the stream, and colluvium and/or flood plain samples where applicable.

All samples collected were sieved and the minus 80 mesh fraction analyzed for Cu, Pb, Zn and Cd. A geologic map of the river basin was compiled from various sources to give stratigraphic and structural control for the area. The stream sediment sampling was conducted at the same time as the water survey portion of the project (Proctor, et al., 1973).

LOCATION

The James River is the main tributary of the White River and is on the eastern fringe of the world renowned Tri-State zinc mining district in southwest Missouri. The basin is 60 miles long, 20 miles wide in the upper two thirds of its length and approximately 30 miles wide in the southern third. It extends from Marshfield on the east to Marionville and Cassville on the west. The basin encompasses about 1460 square miles.

The James River is dammed at Springfield (Lake Springfield) where it is used as cooling water for the municipal stream electric plant. The river drains southward from here into Table Rock Lake, a major recreational area. Water from Table Rock Lake powers a turbo-hydroelectric plant. At Springfield the James River has an average discharge of 176 ft^3/second. This increases to 920 ft^3/second at Galena, Missouri (Homyk and Jeffery, p. 280, 1967).

Springfield is the third largest city in Missouri with over 120,000 people living within the metropolitan area. Several small communities are within the basin and include Marshfield, Seymour, Ozark, Cassville, Galena, Cape Fair, Marionville, and others. Moderate industrial activity exists in and around Springfield. The city operates a sanitary landfill along Jordon Creek near sample 51. A sewage plant is present on Wilson Creek near site 41, figure 1. Outside of Springfield light farming and ranching are the main human activities.

Five major tributaries feed the James River. Finley Creek drains the southeastern section through ranch and farm land. Flat Creek drains the southwestern part near Cassville and empties directly into Table Rock Lake. Crane Creek drains an area immediately northeast of Flat Creek and empties into the lower James River. Crane and Flat Creek drain mainly ranch and farm country. Pearson Creek, just east of Springfield, drains farm, residential and industrial land. Wilson Creek is the main watershed of Springfield and is used to dispose of treated municipal and industrial wastes. All main tributaries drain one or more old mining prospects (figure 2).

In the basin the climate is temperate to humid with an average annual precipitation of 40-44 inches. Average annual runoff is 12-14 inches (Homyk, et al., 1967). The basin topography is in early maturity in the northern quarter with decreasing development to the more youthful stages in the southernmost parts. Relief is correspondingly about 50 feet in the north and to 200 feet or greater in the south.

LITERATURE REVIEW

The earliest geologic studies in the Springfield area were made by Shepard (1898) and Park (1905) and concerned the geology and hydrology

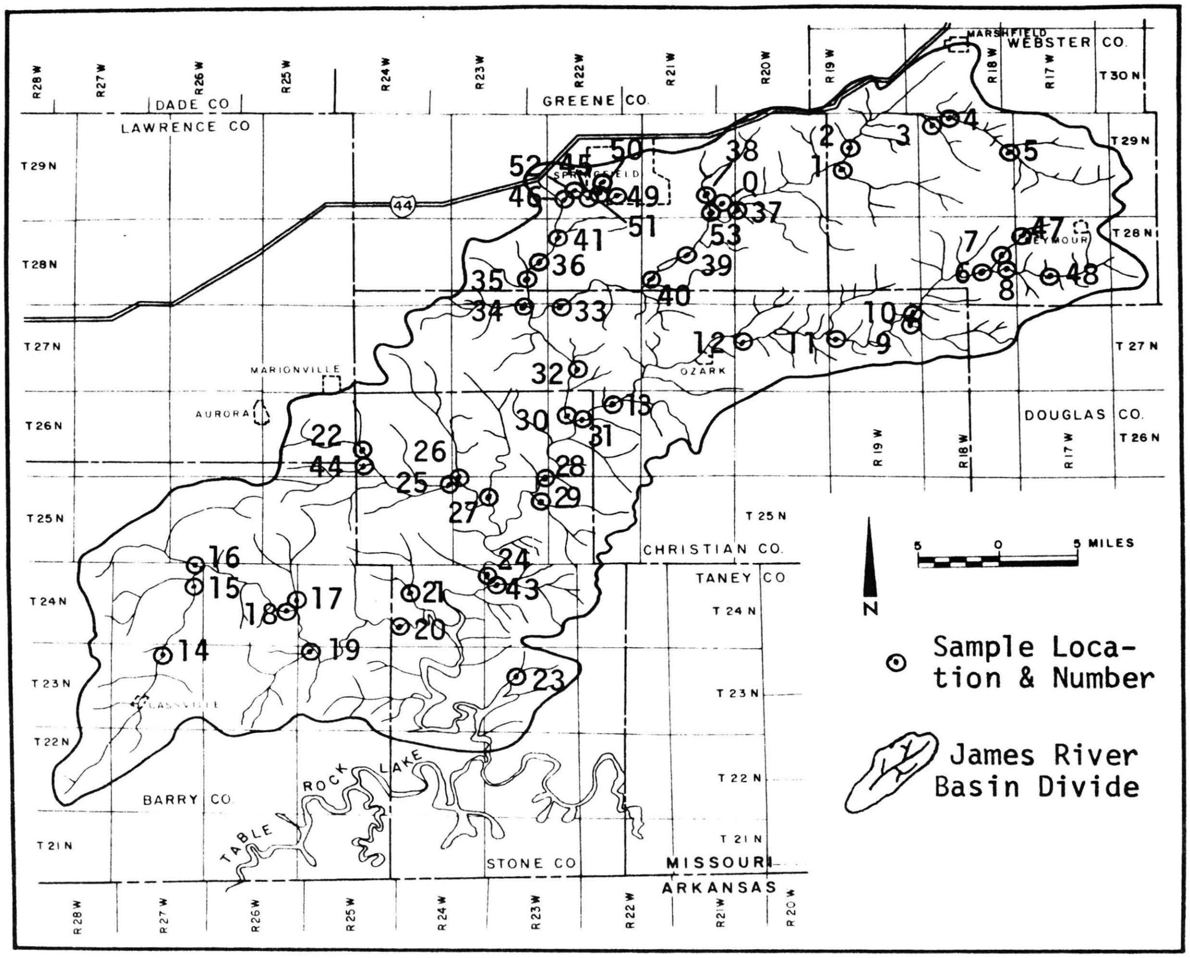

Figure 1. Stream sediment sample locations in the James River basin, Missouri.

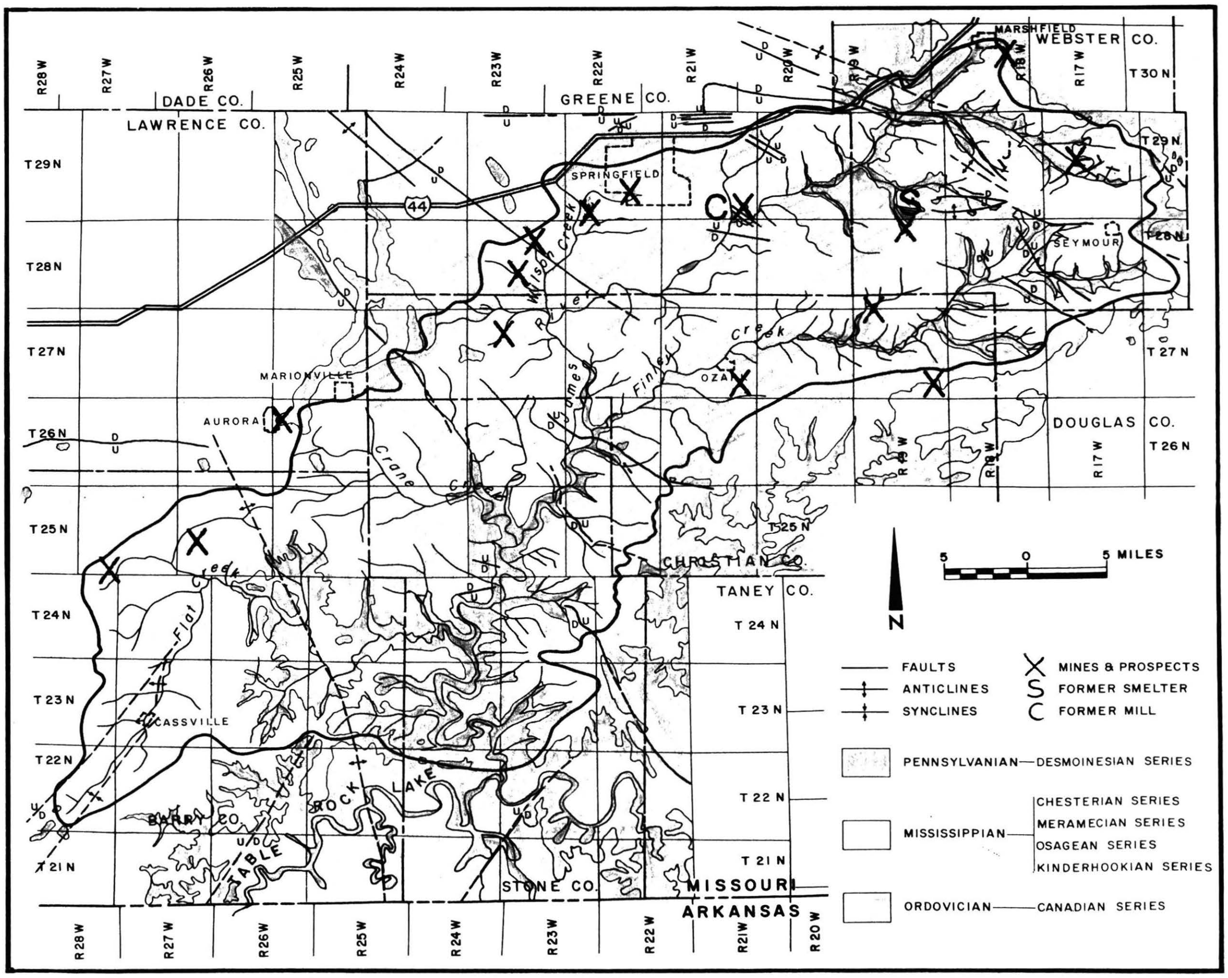

Figure 2. Geologic map with structural features and mineralized areas of the James River basin, Missouri.

of the municipal area. Three geologic reconnaissance maps were made of parts of the river basin by staff of the Missouri Geological Survey (Beveridge, 1970, Fellows, 1970, Clark, 1941). Fellows (1963) showed solution remnants in the Springfield metropolitan areas. The geology between Springfield and Branson, Missouri, was described by Vineyard and Fellows (1967). Surface water supply of the James River basin was discussed in the Mineral and Water Resources of Missouri (Fuller and Knight, 1967, Homyk and Jeffery, 1967). Harvey and Skelton (1968) studied Wilson Creek in relation to waste disposal problems. A James River-Wilson Creek study was cooperatively made by the Federal Water Pollution Control Administration and the Missouri Geological Survey (1969) to investigate flow of ground and surface water and their physical and chemical characteristics. The U.S. Geological Survey completed a reconnaissance survey of the trace metals of the soils, plants, sediments, rocks, and water of the State of Missouri (Miesch, et al., 1971). Proctor, et al. (1973) studied the heavy metal content of water, in the Springfield-Joplin region. Garrison (1973) as part of the latter project completed a thesis on the heavy metal content of waters in the Joplin area. Likewise, Williams (1973) reported on heavy metal content of waters in the Springfield area. Proctor and Lance are completing a study on the heavy metal content in the surface waters of the James River basin.

In related research, Bolter and Wixson (1969, et sequ.) studied waters in the "New Lead Belt". Hornsnail et al. (1969) showed variations of heavy metals in drainage sediments due to changes in the secondary environment. Nigrini (1971) showed the deposition and transport of heavy metals in the secondary environment.

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Thanks also go to Richard Lance for his help and humor in taking the field samples and in working in mutual interest on this project. A large amount of appreciation is extended to my wife for her help in the typing of this paper and her patience. Thanks are also extended to my friends who helped in the drafting of maps and figures for this paper.

GEOLOGIC SETTING OF THE BASIN

STRATIGRAPHY

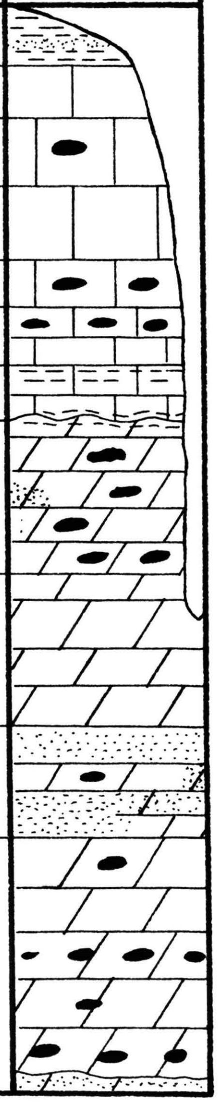
The James River basin comprises an area of mainly Mississippian carbonates with Ordovician carbonates cropping out to the south and east. The Mississippian rocks underlie the broad slightly sloping Springfield Plateau which shows karst topography.

The following stratigraphic descriptions are much condensed descriptions from the Stratigraphic Succession of Missouri (1961) and the Guidebook to the Geology Between Springfield and Branson Missouri (1967), and from personal communications with Dr. Larry Fellows and Dr. T. L. Thompson of the Missouri Geological Survey (1973). A summary stratigraphic column is shown in figure 3.

Ordovician rocks present at the surface within the river basin are of the Canadian Series and include the Jefferson City and Cotter Formations.

The Jefferson City Formation is light brown to brown, medium to fine crystalline dolomite and argillaceous dolomite with lenses of orthoquartzite, conglomerate, oolitic cherts and shale locally present. The formation is thickly-bedded to massive. The base of the formation weathers with a coarsely pitted surface. Insoluble residues from the formation contain siliceous spicules. The average thickness of the Jefferson City Formation is 200 feet.

The Cotter Formation is light gray to light brown, medium to finely crystalline cherty dolomite; medium to thinly-bedded and contains thin intercalated beds of green shale and sandstone. The Lower Cotter is non-cherty and contains echinoderm fragments. The middle part is



SYSTEM	SERIES	FORMATION	LITHOLOGY
PENN	Desmoinesian	CHEROKEE GROUP	
MISSISSIPPIAN	Chesterian	CARTERVILLE FORMATION	
	Meramecian	WARSAW FORMATION	
	OSAGEAN	BURLINGTON/KEOKUK LIMESTONE	
		ELSEY FORMATION	
		PIERSON/REED SPRING FORMATION	
	Kinderhookian	NORTHVIEW/COMPTON FORMATION	
ORDOVICIAN	CANADIAN	COTTER DOLOMITE	
		JEFFERSON CITY DOLOMITE	
		ROUBIDOUX FORMATION	
		GASCONADE DOLOMITE	

Figure 3. Stratigraphic section of James River basin. Exposures mainly include units above the Roubidoux Formation.

oolitic chert with large silicious oolites. The Upper Cotter is shaley and contains small quartz masses and brown quartzose oolitic chert. Twenty miles south of Springfield the Cotter was slightly folded and faulted prior to the deposition of the Chattanooga shale. It is thought that the folded Cotter represents drag along a pre-Chattanooga or pre-Bachelor fault with recurrent movement at a later time. The Cotter resembles the Jefferson City Formation and is difficult to separate from it. Average thickness is 200 feet.

The Chattanooga Formation is a fissile, black, slightly arenaceous, spore-bearing shale with a petroliferous odor. Joints in the unit are obliquely inclined to the bedding and the shales are easily weathered. Thickness ranges from 3-6 feet in Green and Christian Counties, and 2-3 feet along James River near Nixa. The Chattanooga shale has been much disputed as to whether it is Devonian or Mississippian and remains unclassified in this area.

The Mississippian system is divided into three series: The Kinderhookian, Osagean, and Meramecian, respectively. The Kinderhookian Series lies upon the Ordovician Cotter Formation throughout the basin. The Kinderhookian Series includes the Bachelor, Compton and Northview Formations.

The Bachelor Formation has two members. The lower is greenish, quartzose sandstone cemented with calcite; characterized by included pebbles and cobbles of Cotter-like chert, black phosphatic pebbles, and abraded fish teeth. The upper member is sandy grayish-green shale. Average thickness is 5-18 inches.

The Compton Formation is a finely crystalline to sublithographic somewhat crinoidal limestone. It is thin, wavy, nodular-bedded and separated by green shale partings. Some chert is present, and it is not abundantly fossiliferous. The basal part of the Compton is sandy and south of Springfield it becomes argillaceous. Average thickness is 20 feet.

The Northview Formation is brown, buff, bluish green siltstone that is massive when fresh and weathers rapidly to green shale or silty clay. Locally pyritized and limonitized internal molds of brachiopods occur. In Greene and Webster Counties, the lower part is shale and the upper section is siltstone with shale. Average thickness is 80 feet. The formation is absent south of central Stone and Barry Counties.

The Osagean Series includes the Pearson Formation, Reed Springs Formation, Elsey Formation, Keokuk Limestone, and Burlington Limestone.

The Pierson Formation is made up of gray, crinoidal limestone. In south Greene County and southwest Missouri it consists of two major units. The lower unit is medium to massively-bedded, brown dolomite, 5-20 inches thick. The upper unit is a cherty limestone and dolomitic limestone medium-bedded with cream colored chert nodules. This formation thins northward. Southward from Greene County the Pearson Formation thickens and the upper part becomes more cherty and the lower portion more calcareous and thin-bedded. In southern Stone and Barry Counties, the upper layer of chert varies in color and becomes mottled with yellowish brown and brick red stains. Crinoidal fragments increase in number southward and the limestone units become more argillaceous and mottled with dark red and limonitic yellow stains. The average thickness is 20-35 feet.

The Reeds Spring Formation consist of alternating dark gray, finely crystalline, sparsely fossiliferous limestone. It contains irregular beds and discontinuous bands of dark gray to bluish chert nodules which make up 1/3 - 2/3 of the formation and are most abundant in the upper portions. The base of the formation is marked by thin, green to brown sandy shale. The Reeds Spring Formation does not extend into or north of Greene County and is not known east of Christian, Stone and Taney Counties. The average thickness is 100 feet.

The Elsey Formation is a cherty gray limestone, finely crystalline and sparsely fossiliferous. The chert occurs as smooth to slightly irregularly shaped nodules flattened parallel to the bedding or as discontinuous beds mottled brown and gray when fresh or cream to white and tripolitic when weathered. In the Springfield area the Elsey limestone rests on the Pierson Formation and is overlain by Burlington. To the south and southwest the Elsey Formation occurs above the Pierson without the Burlington. This formation is also known as the Grand Falls Formation. Average thickness is 30 feet.

The Keokuk Limestone is very similar to the Burlington. It is bluish-gray; medium to coarsely crystalline; medium-bedded; and contains abundant amount of light gray bedded and nodular chert. The Keokuk is finely crystalline in southwest Missouri and contains crinoids. Chert occurs above and below an oolitic limestone layer and weathers to a matted appearance. Average thickness of the formation is 100 feet and the formation lies on the older Elsey or Reeds Spring Formation.

The Burlington Limestone is gray to white, thick to massively bedded, cherty in its upper layers and very coarsely crystalline. It is fossiliferous containing mainly crinoids and some corals. The

Burlington Limestone pinches out in south Barry County. Average thickness is 100 feet.

The Meramecian Series is represented in only one square mile within Springfield. This is a fifteen foot thick remnant of the Warsaw Formation. The Warsaw is a cherty limestone containing cryptozoans and thin shale partings.

The Chesterian Series, part of the Upper Mississippian, occurs in small amounts in the extreme western part of Lawrence and Barry Counties, outside the drainage basin. Some Pennsylvanian rocks are also present in the extreme western parts of these counties and in eastern Greene County. The latter system consists of formations of the Cherokee Group of shaley sandstones and limey shales.

The river basin is faulted. The faults bear mainly north 65° west in the south and north 25° west in the north and have a north 55° east complementary set (figure 2). The northeastern portion of the basin is also faulted. Vertical displacements occur on the Strafford Fault north of Springfield and at the Diggins Fault at Seymour of up to 140 feet. An anticline and syncline occur in Township T29N, R18W and trend N 5° E, N 45° W. The Osage-Verona Anticline lies south of Aurora and trends N 25° W. The Cassville Anticline occurs north of Cassville and trends a N 20° E direction. A syncline trending N 20° E lies south of Cassville.

MINERALIZATION

Sphalerite - galena deposits occur in some of the faulted areas in varying quantities in all lithologies. The Burlington Keokuk Formation contains the highest number of mineralized occurrences (Shepard, 1898, p. 160). Marcasite (FeS_2) is also a prominent mineral. Copper carbonates, cerussite ($PbCO_3$), limonite ($HFeO_2$) and hemimorphite ($Zn_4SI_2O_7(OH)_2 \cdot H_2O$) are known from the deposits. Greenockite (CdS) is an uncommon mineral in sphalerite deposits (Kiilsgaard, et al., 1967, p. 56).

Known distributions of mining prospects are shown in figure 2. Lead mineralized areas occur in upper Crane and Flat Creeks (McCracken, 1971). These areas also have some associated zinc and copper occurrences (Shepard, 1898). Old mining prospects where mineralization occurs are located along Wilson Creek, upper Wilson Creek (Jordan Creek), Pearson Creek (just east of Springfield), the upper James River and middle Finley Creek. Small occurrences of galena and sphalerite are said to exist in faults and at random locations in the different stratigraphic units (Shepard, 1898). An old concentrator site is located on Pearson Creek and an old smelter site is located on the upper James River which may add metal contributions to the sediments. Flat and Finley Creeks are considered low in mineralization present along the stream course in comparison to Wilson Creek which has evidence of mineral deposits throughout its total length.

STREAM SEDIMENTS

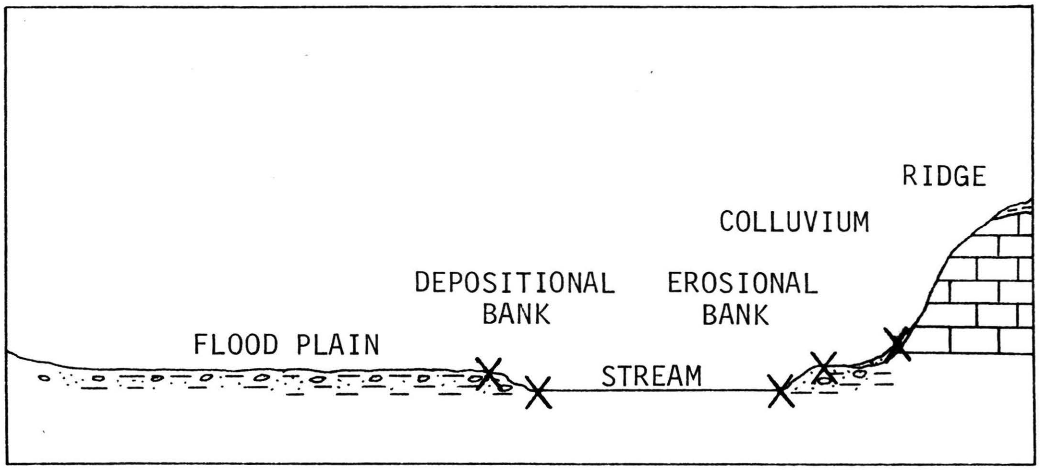
The stream sediments observed consisted of two basic types. Most of the sediments found in the active channel were gravels varying in size from cobbles, ~5 cm across to fine sandy silts. Sediments under the average water level are well washed containing little fines. Sediments found on the banks in the zone of seasonal water fluctuations are more sandy with less cobble size gravel and containing a larger amount of silts. The cobbles are mainly chert, sands and silts are silica with some clays and organic material present (table 4). The second type of sediment contains mainly finer sands and silts with little or no gravel size particles. These occurred in areas of better developed flood plains with agricultural activity. The silty stream sediments also contained numerous amounts of small organic material and clay particles.

SAMPLING AND ANALYTICAL METHODS

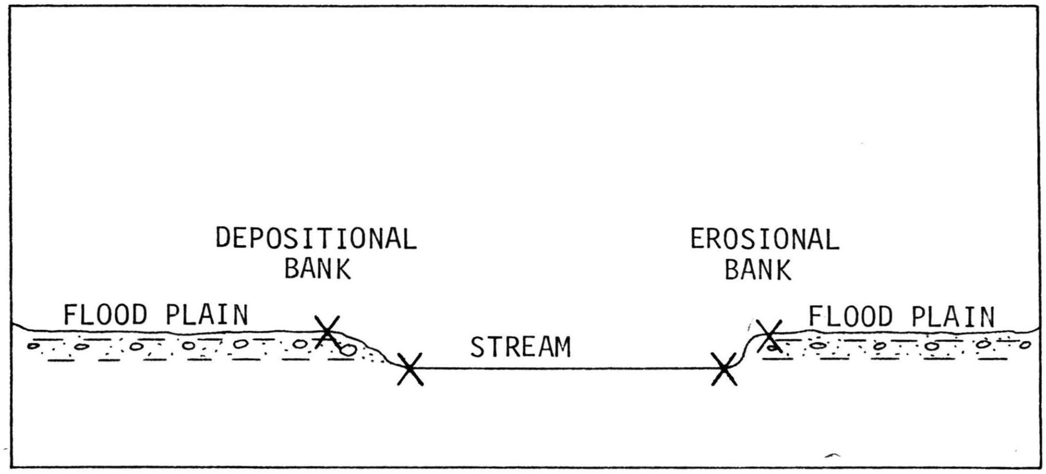
Sediment samples were collected at selected points along the active stream channels in the basin. The stream sediment sites were of a reconnaissance type to permit more random-like samples of the basin population. Fifty two (52) different sites represent the confluences of streams and rivers, streams and creeks, and the intersections of linear flow at points of vehicle access midway between major confluences. A sample (site Q) was also taken from a dry creek bed draining an old prospect dump. Locations of the various samples are shown in figure 1.

Scoop samples of approximately 100 grams of sediment were gathered from the depositional stream side at or below the present water line. During the winter and spring sampling phases, high water made sampling impossible in the main course of several streams and samples were obtained from the high water level depositional material rather than the bottom of the main channel or its banks. Profile samples across the channel were collected during the spring sampling period. These profiles were at points where unusual metal content had been determined from summer and winter collection sets. The cross stream sediment profiles consisted of a flood plain sample, adjacent bank and stream samples, a fast water sediment sample, an erosional bank sample and a colluvium sample where applicable (figure 4).

All sediment samples were collected upstream from bridges and other obvious areas of human activity. The stream sediment cross profiles were collected to test the validity of the single sample



Cross section of typical profile for sampling locations numbers 6 and 53.



Cross section of typical profile for flood plain locations numbers 30, 36, and 51.

Figure 4. Stream sediment profile sampling points, given in cross sections of stream channel type.

previously obtained and to show possible variance of heavy metals in different parts of the stream channel. After initial sampling, upper Wilson Creek, Pearson Creek, and upper Finley Creek were resampled to better identify possible sources of the heavy metals. This sampling also provided comparisons of a known mineralized stream section with stream sections in low mineralized and non-industrialized areas.

The first and second samples were placed in plastic bags. These retained a large amount of moisture and required later drying before sieving. These were dried in clean beakers overnight in an oven and then disaggregated. The third sample set was placed in heavy paper bags. This facilitated drying in the open air before reaching the sieving stage. Some drying was needed and was accomplished by turning on a 200 watt light bulb near the bags for a 15 hour period. All samples were sieved in a stainless steel U.S. Standard sieve set to recover the minus 80 sieve fraction. The minus 80 mesh fraction was chosen because the absorption effects of clay particles in this size range are at the optimum level (Perhac and Whelan, 1972, Hawkes and Webb, 1962). Approximately 50-100 grams of sand and gravel type sediments were required to obtain 1 gram of the minus 80 mesh fraction.

Every piece of laboratory glassware or teflonware was washed in HCl wash solution, rinsed with distilled water twice after each use, and then washed again using the same procedure before each later use. Some bottles were soaked in sodium ethylenediamine tetraacetate solution overnight and then sent through the wash cycle. New bottles were assumed "clean" of heavy metals and tested using blank solutions.

One gram of -80 mesh sample was placed in a clean beaker to which

5 ml of concentrated nitric acid was added along with approximately 5 ml of demineralized water. The mixture was heated in a sand bath for about thirty (30) minutes and allowed to boil. Five ml more of concentrated HNO_3 was added with enough water to bring it to the approximate original volume. The mixture was again allowed to boil for 30 minutes or until a reduced volume was evident without being dry. During heating periods the solutions were stirred twice. The leaching process of heavy metals in hot nitric solution was regulated by controlling the amount of nitric acid in solution at the different preparation stages with 15 ml nitric acid used in the total 100 ml volume of solution. Next, the hot solutions were filtered through Whatman No. 1 qualitative paper filter. The unfiltered material was rinsed with demineralized H_2O and 5 ml of concentrated nitric acid. The volume was brought up to 100 ml with demineralized water in a volumetric flask, and the leach solution placed in a clean plastic bottle. A blank was prepared during this process to allow determination of the inherent analytical errors involved by preparation through this procedure. Inherent errors involve possible contaminations from the bottles, the funnels, the filter paper, the nitric acid and the demineralized water. Also, error may be introduced in measuring the volumes of acid and water and in the varying mechanical conditions of the atomic absorption unit. The latter errors were consistent for each. The lower detection limit was determined as the value of the blank solution prepared with the sediment samples and was set at zero for that run.

Standards were prepared by dilution with demineralized water and nitric acid from 1000 ppm reference solutions (after Ward, et al., 1969).

The solutions were run by standard procedure on a Perkin-Elmer 303 Atomic Absorption spectrophotometer with strip chart recorder output.

GEOCHEMICAL RESULTS OF STREAM SEDIMENT SAMPLES

TRACE METAL VALUES

Results of trace element analyses of the minus 80 mesh stream sediments for copper, lead, zinc and cadmium are presented in table 1. Specific locations and pH at sample sites during sediment sampling collections are given in Appendix I. Values are listed in parts per million. Values in table 1 listed in the tables are the highest and lowest metal contents at a sample site. The latter may not necessarily be exactly the same point for a second sample due to fluctuating water levels and changing stream conditions. If a site was sampled only once, results are listed as a minimum value. Values below analytical detection limits are given as 0. Sample sites of the same stream systems are grouped together for convenience or review and interpretation. Table 3 also lists means and standard deviations for the whole basin and the streams within it using a statistical program developed by Garrison (1973).

Heavy metal distributions along a linear line of the streams in the basin together with a schematic geologic section are shown in figures 5, 6, 7, 8, and 9. The vertical log scale for the values is in parts per million. The horizontal scale is 1:500,000 and no vertical scale is implied in the schematic geologic section. The Cu, Pb, Zn, and Cd distributions of the fine fraction stream sediments throughout the basin are shown in figures 10, 11, 12, and 13.

Average values of Cu, Pb, Zn, and Cd in limestones are 20 ppm, 5-10 ppm, 50 ppm, and 0-.3 ppm, respectively, (Rankama and Sahama, 1950). Hawkes and Webb (1962)give Cu as 5-20 ppm, Pb as 5-10 ppm,

		Range ppm												NO. OF TIMES SAMPLED
		Zn			Cd			Cu			Pb			
		MIN	MAX	AVG	MIN	MAX	AVG	MIN	MAX	AVG	MIN	MAX	AVG	
James River	1	6.5		6.5	0.57		0.57	4.2		4.2	25.9		25.9	1
	2	23.2		23.2	0		0	4.6		4.56	10.3		10.3	1
	3	30.8		30.8	0.51		0.51	6.6		6.6	25.9		25.9	1
	4	41.6		41.6	0.76		0.76	6.2		6.2	28.4		28.4	1
	5	63.4		63.4	0.64		0.64	6.4		6.4	29.0		29.0	1
	24	35.9		35.9	0		0	4.6		4.6	30.4		30.4	1
	28	110.7		110.7	0.76		0.76	28.6		28.6**	97.9		97.9	1
	†30	69.0	146.1	91.7	0.28	1.25	0.63	0	27.9	7.2	34.9	91.1	57.2	6
	32	18.9	106.7	62.8	0	0.7	0.35	12.7	14.0	13.4	47.1	93.6	70.4	2
	33	47.2		74.2	0.35		0.35	15.2		15.2	33.4		33.4	1
	37	25.2	56.7	40.9	0.04	0.30	0.17	11.5	17.1	14.3	28.8	106.4	67.6	2
	38	197.7	533	365.3**	2.27	3.04	2.66	5.9	27.0	16.4	57.7	170.2	114.0	2
	39	113.3		113.3	0.55		0.55	7.9		7.9	127.7		127.7	1
	40	116.7		116.7	1.35		1.35	25.5		25.4	93.6		93.6	1
	†53	350	607	514.8**	2.22	22.75	11.61*	0	15.6	7.2	184.0	593	388.8*	6
		M.=99.7	S.D.=135.4		M.=1.4	S.D.=2.7		M.=9.9	S.D.=8.0		M.=75.6	S.D.=87.8		
Wilson Creek	34	10.1	78.3	44.2	0	1.4	0.7	2.9	13.5	8.2	16.7	153.2	84.9	2
	35	251	422	336.5*	2.51	2.61	2.56	40.5	55.1	47.8*	212.8	296.0	254	2
	†36	80.5	419	292.3*	0	3.28	1.68	0	87.3	20.5	58	437.5	299.8	6
	41	256.9		256.9	2.51		2.51	50.2		50.2*	437.5		437.5*	1
	45	245.9		256.9	3.31		3.31*	51.8		51.8*	562.5		562.5*	1
	46	278.0		278.0*	3.34		3.34*	97.6		97.6*	500		500*	1
	49	232		232	3.16		3.16	35.9		35.9*	488		488*	1

Table 1. Zinc, cadmium, copper, and lead stream sediment sample values in ppm.

		Range, ppm												NO. OF TIMES SAMPLED
		Zn			Cd			Cu			Pb			
		MIN	MAX	AVG	MIN	MAX	AVG	MIN	MAX	AVG	MIN	MAX	AVG	
Wilson Creek	50	380		380*	5.31		5.31*	80.2		80.2*	520		520*	1
	†51	147.5	487	356.7*	0.91	4.31	2.49	1.7	63.3	18.1	98.6	562	347.9*	5
	52	282		282*	5.18		5.18*	34.2		34.2	188.2		188.2	1
		M.=271.6 S.D.-92.8			M.=3.0 S.D.-1.4			M.=44.4 S.D.=27.8			M.=361.3 S.D.=164.0			
Finley Creek	†6	16.8	36.9	36.9	0	0.31	0.13	0	11.6	6.6	16.8	36.9	27.0	5
	7	38.3		38.3	0		0	3.2		3.2	85.1		85.1*	1
	8	116.7		116.7**	3.28		3.28*	56.4		56.4**	42.6		42.6	1
	9	30.3		30.3	0.16		0.16	4.6		4.6	33.6		33.6	1
	10	610		610**	61.8		61.8*	9.1		9.1	>570		>570**	1
	11	10.5		10.5	0.44		0.44	5.2		5.2	15.5		15.5	1
	12	23.2		23.2	1.01		1.01	5.8		5.8	20.7		20.7	1
	13	68.3		68.3	0		0	14.3		14.3**	63.8		63.8**	1
	31	45.1	78.3	66.5	0	0.11	0.06	0	13.3	6.3	18.2	59.6	37.1	3
	47	28.6		28.6	0.69		0.69	7.3		7.3	33.6		33.6	1
	48	5.4		5.4	0.72		0.72	5.2		5.2	20.7		20.7	1
		M.=39.1# S.D.=32.2#			M.=.6# S.D.=.98#			M.=6.8# S.D.=3.1##			M.=36.9# S.D.=21.9#			
Flat Creek	14	110.2		110.2	0.75		0.75	9.5		9.5*	33.6		33.6**	1
	15	103.9		103.9	1.65		1.65*	6.5		6.5	21.2		21.2	1
	16	193.0	459.0	376.0**	0.63	1.29	0.96	0	9.6	4.8	19.7	24.2	22.0	2
	17	0	24.0	12.0	0		0	3.0		3.0	15.2		15.2	1
	18	105.7	106.1	105.9	0.09	0.96	0.53	3.7	7.5	5.6	16.7	18.1	17.4	2
	19	47.2		47.2	0.43		0.43	4.6		4.6	22.8		22.8	1
	20	28.3		28.3	1.09		1.09	7.1		7.1	16.7		16.7	1
		M.-111.9 S.D.=123.2			M.=.8 S.D.=.56			M.=5.1 S.D.=2.8			M.=33.6 S.D.=10.7			

Table 1. Zinc, cadmium, copper, and lead stream sediment sample values in ppm. (continued)

		Ranges, ppm												NO. OF TIMES SAMPLED
		Zn			Cd			Cu			Pb			
		MIN	MAX	AVG	MIN	MAX	AVG	MIN	MAX	AVG	MIN	MAX	AVG	
Crane Creek	22	91.3		91.3	1.01		1.01	6.2		6.2	23.3		23.3	1
	25	72.3	194.1	145.3*	0	0.91	0.49	0	13.97	6.8*	15.2	48.6	30.2	3
	26	95	142.9	118.9	0.48	0.65	0.57	0	1.5	0.8	15.2	85.1	50.1	2
	27	3.1	18.3	10.7	0	0.24	0.12	0	2.9	1.4	10.6	42.6	26.6	2
	44	14.1		14.1	0.73		0.73	5.2		5.2	37.7		37.7	1
		M.=76.1 S.D.=61.2			M.=.8 S.D.=.56			M.=4.1 S.D.=2.8			M.=33.6 S.D.=10.7			
Others	21	18.9		18.9	0		0	7.1		7.1	16.7		16.7	1
	23	9.4		9.4	0.44		0.44	5.2		5.2	24.3		24.3	1
	29	12.6	27.0	14.8	0	0.57	0.29	0	0.79	0.4	18.2	51.1	34.7	2
	43	15.3		15.3	0.88		0.88	0		0	49.4		49.4	1
	Q	24.6		24.6	0		0	0		0	23.5		23.5	1

* above 1 S.D. + Mean

** above 2 S.D. + Mean

† including profiles

\# without no. 10

\## without no. 8

Table 1. Zinc, cadmium, copper, and lead stream sediment sample values in ppm. (continued)

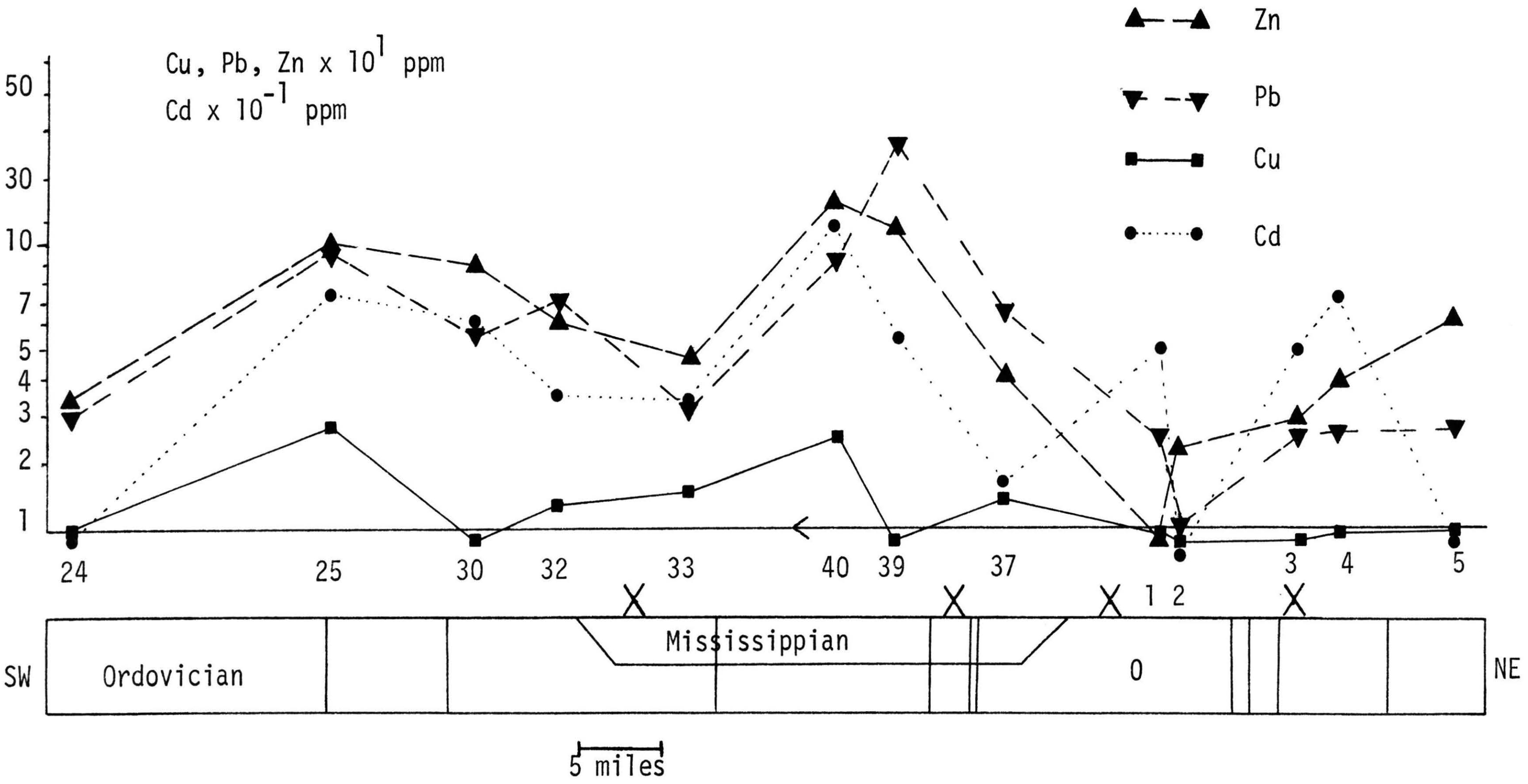


Figure 5: Longitudinal profile of the James River with Cu, Pb, Zn and Cd trace metal values of stream sediments in ppm.

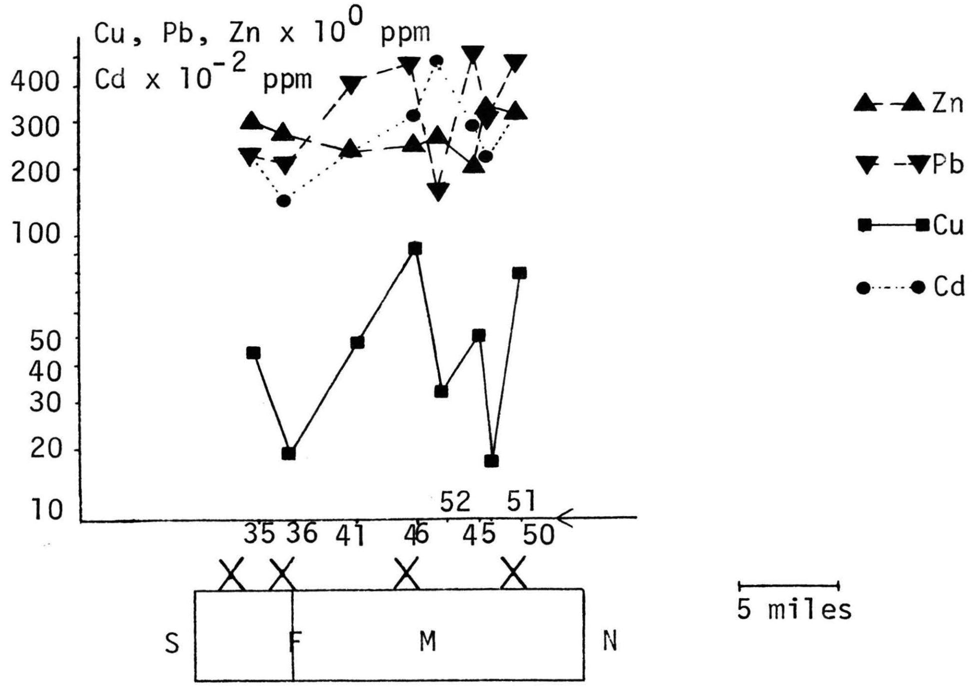


Figure 6: Longitudinal profile of Wilson Creek with Cu, Pb, Zn and Cd trace metal values of stream sediments in ppm.

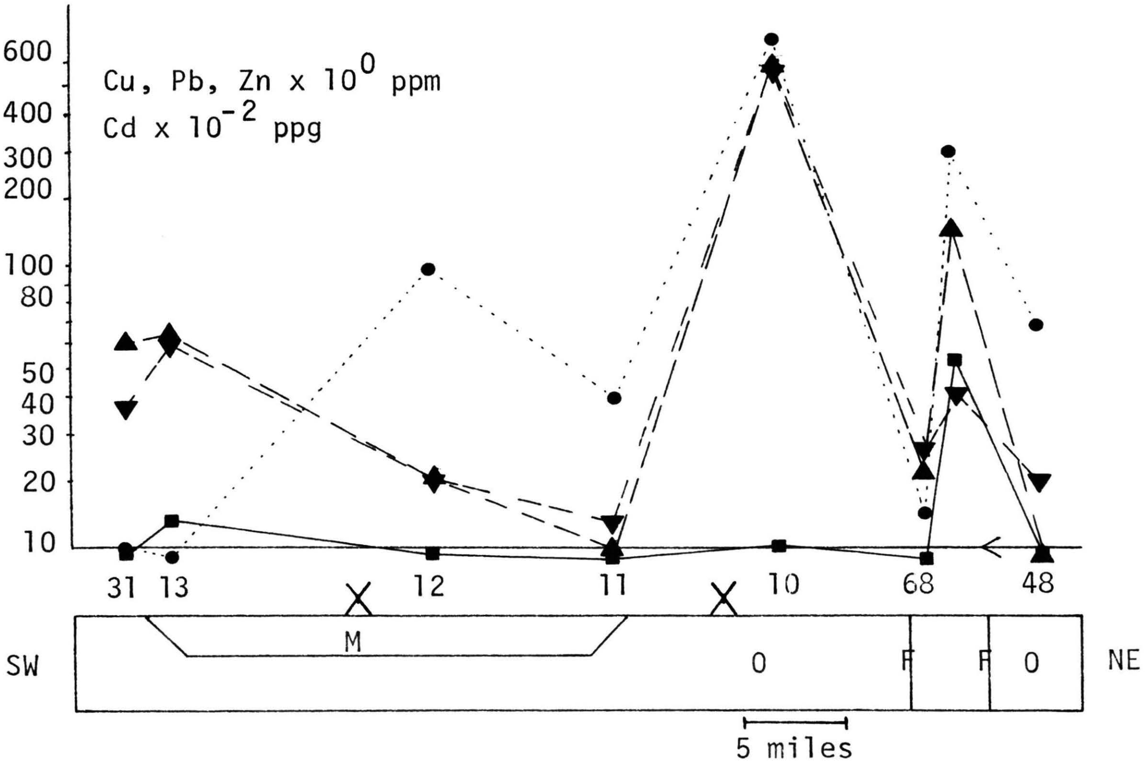


Figure 7: Longitudinal profile of Finley Creek with Cu, Pb, Zn and Cd trace metal values of stream sediments in ppm.

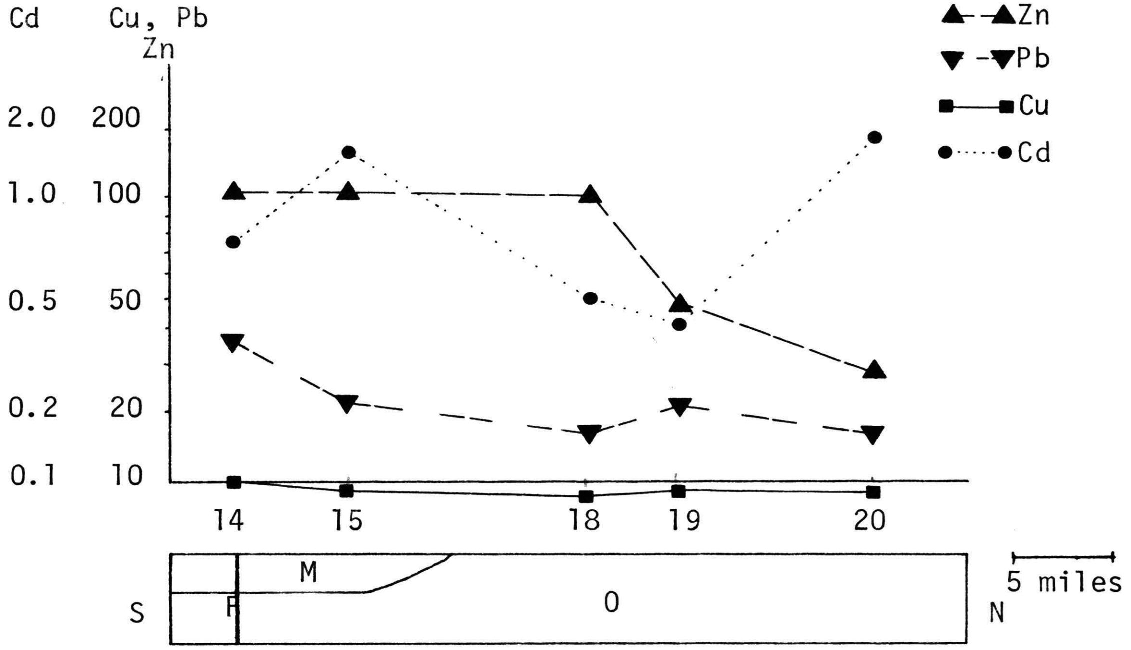


Figure 8 : Longitudinal profile of Flat Creek with Cu, Pb, Zn and Cd trace metal values of stream sediments in ppm.

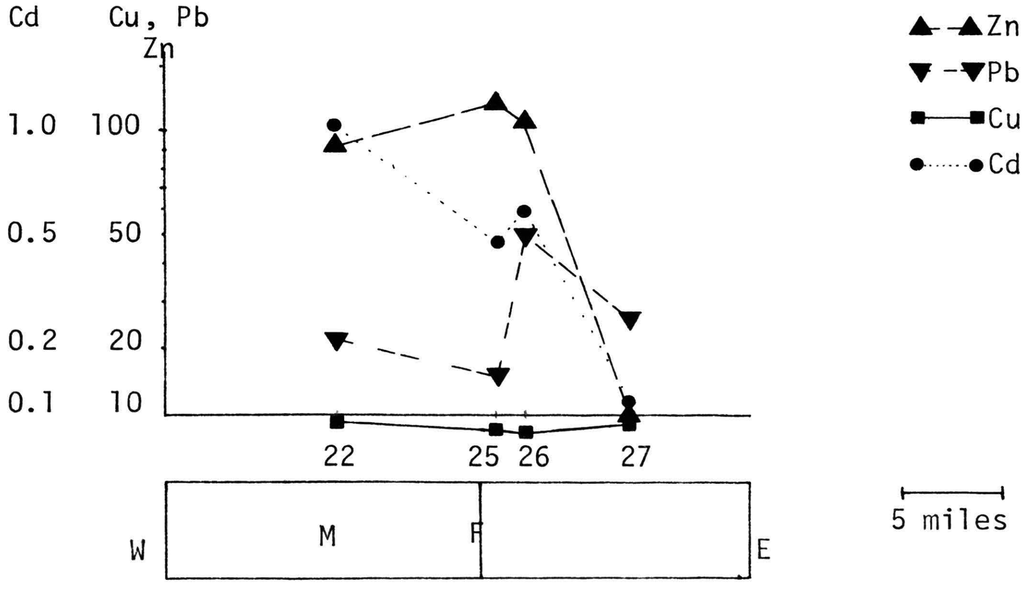


Figure 9: Longitudinal profile of Crane Creek with Cu, Pb, Zn and Cd trace metal values of stream sediments in ppm.

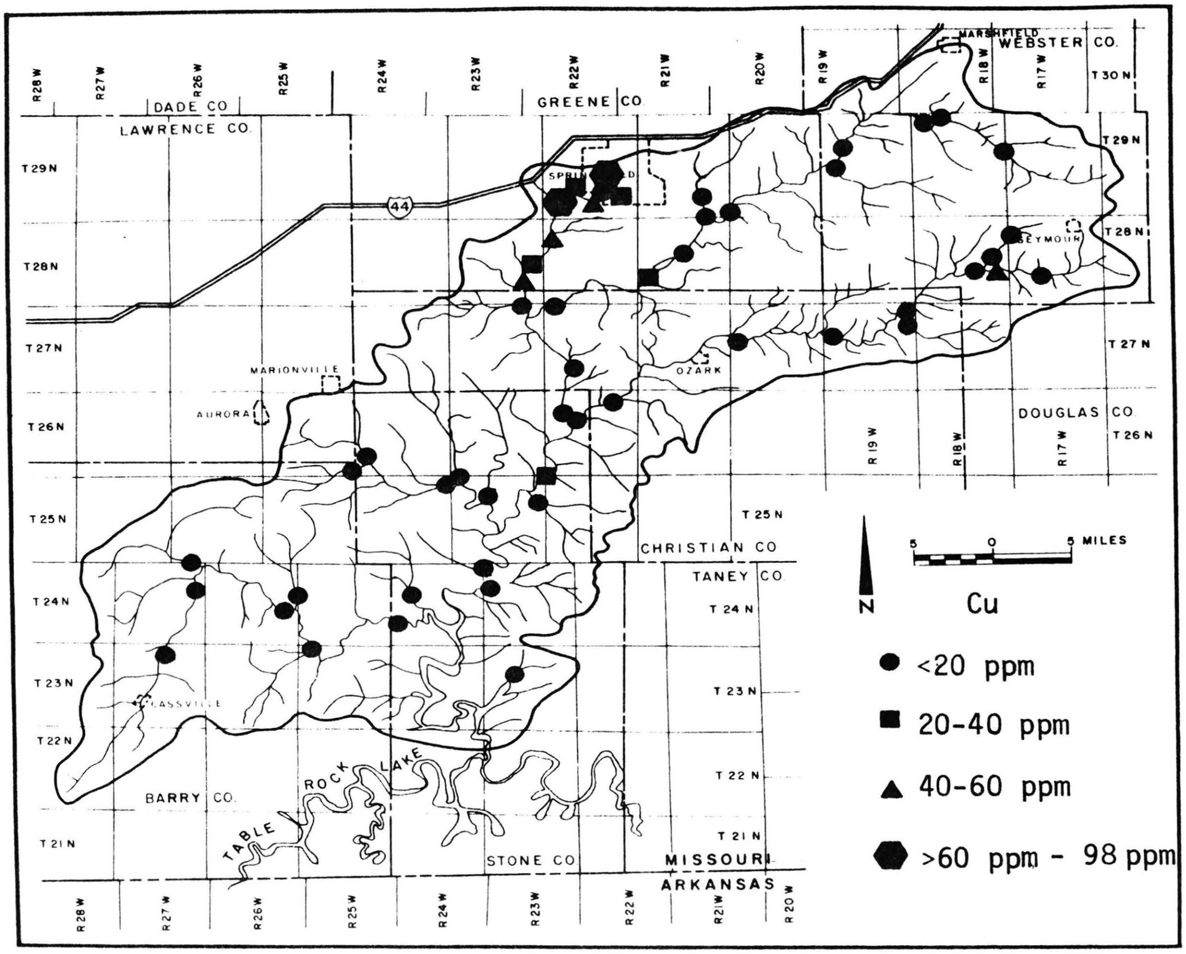


Figure 10. Copper distribution in stream sediments, James River basin, Missouri.

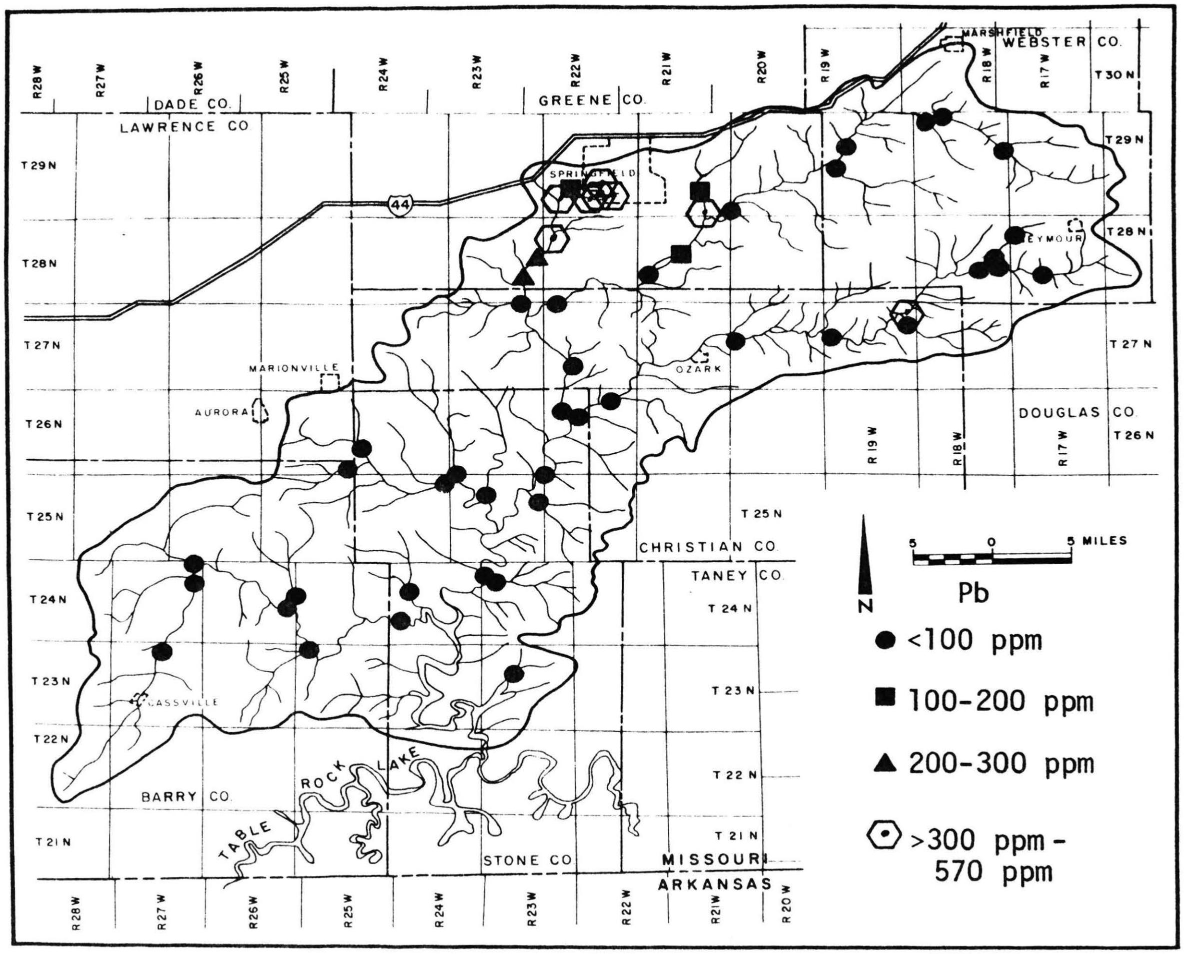


Figure 11. Lead distribution in stream sediments, James River basin, Missouri.

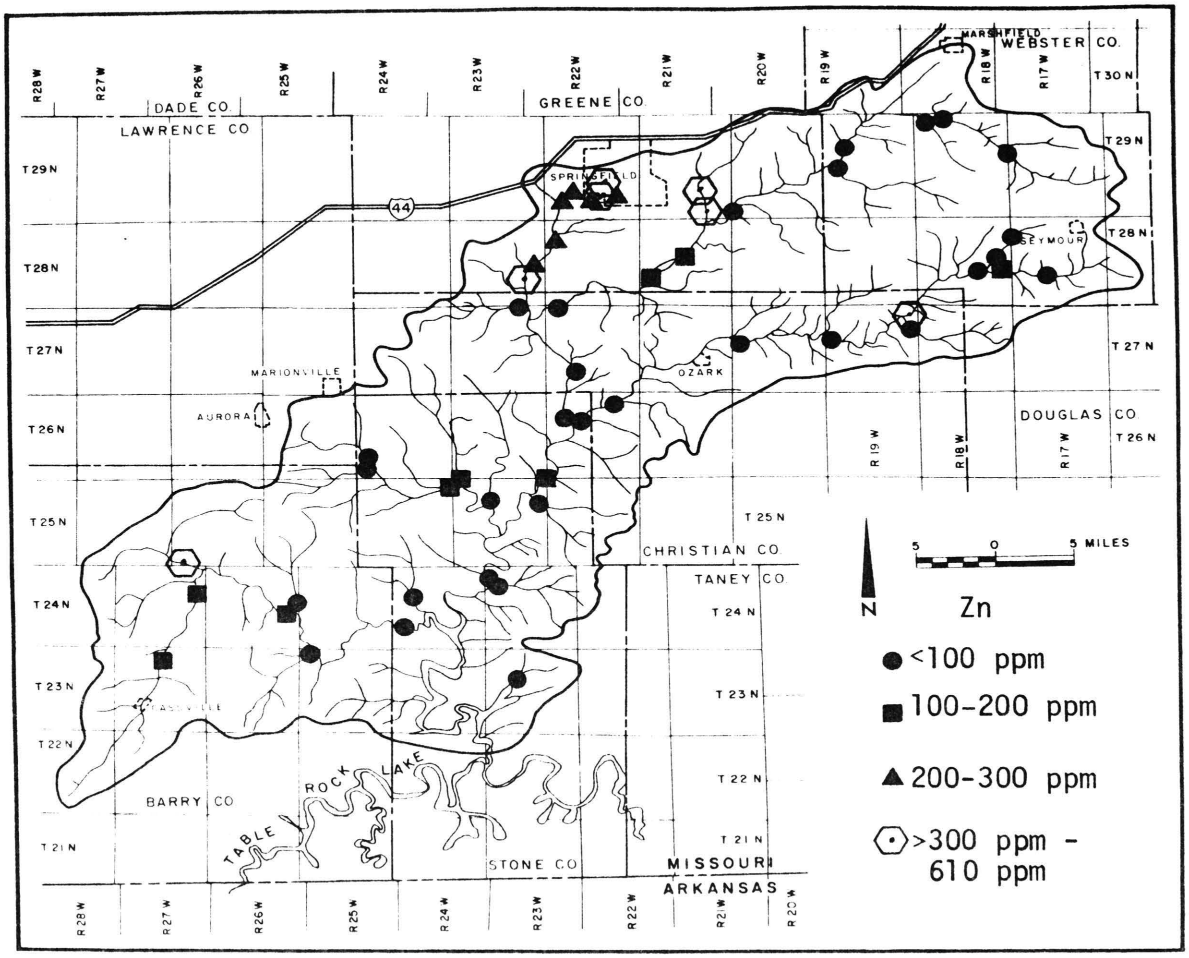


Figure 12. Zinc distribution in stream sediments, James River basin, Missouri.

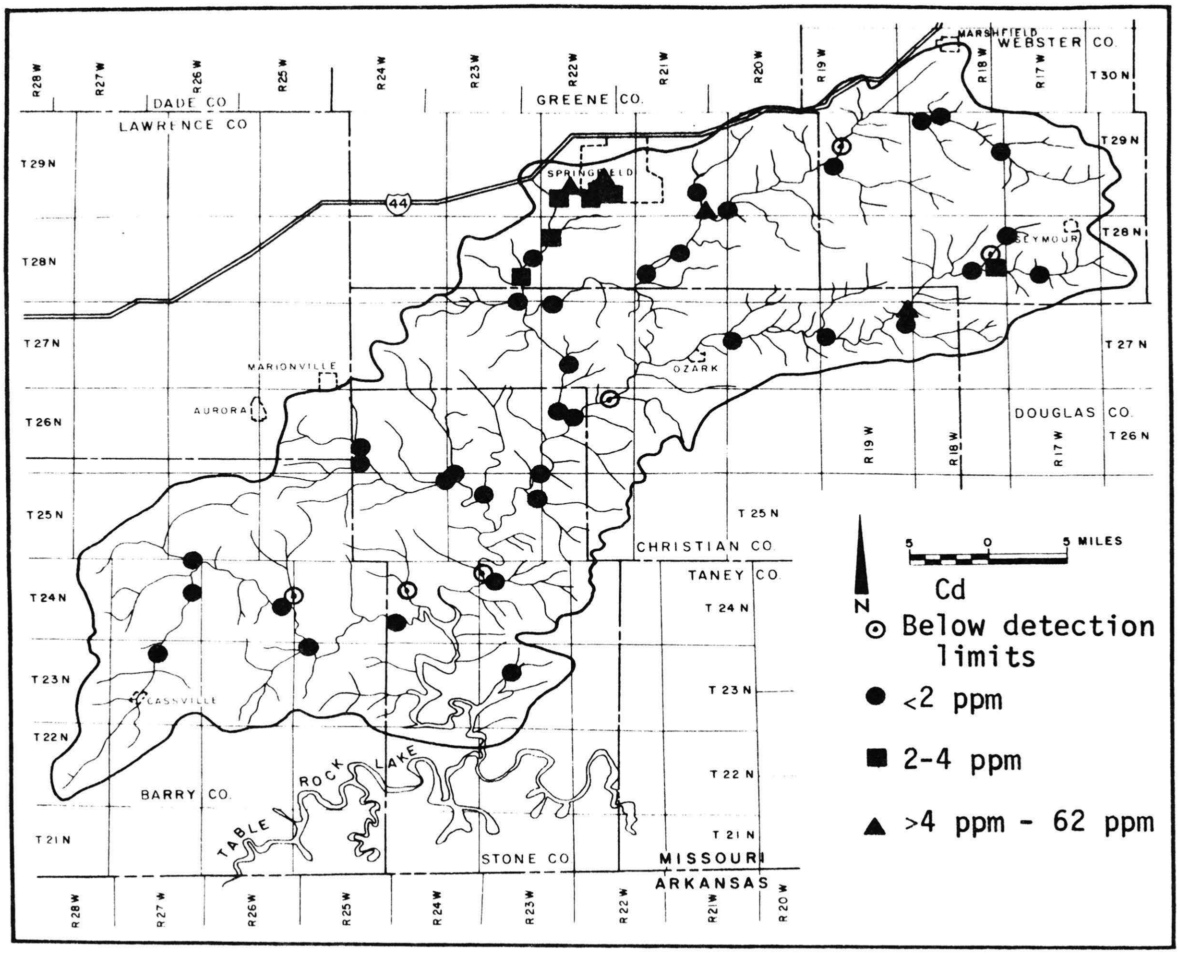


Figure 13. Cadmium distribution in stream sediments, James River basin, Missouri.

Zn as 4-20 ppm and Cd as 0.3 ppm in limestone in non-mineralized areas. Because limestones in the James River basin locally contain small deposits of Cu, Pb, Zn, and Cd, average values for these metals might be higher than those listed. For the entire James River basin, the average lead value in the minus 80 fraction stream sediments is 119 ppm, zinc is 128 ppm, copper is 16 ppm, and cadmium is 1.9 ppm.

The James River -80 fraction sediments display noticable variations in trace metal values within the stream (refer to figure 5). The upper James River before the confluence of Pearson Creek ranges from 7 ppm to 63 ppm Zn and averages 35 ppm. The zinc content in this fraction increases to 113 ppm at site 39, just below the confluence. Zinc values remain between 47 and 91 ppm in the fine fraction for the remainder of the lower James River. No noticeable increases were noted from Wilson Creek, Crane Creek, or Finley Creek. Cadmium values are consistently below 1 ppm directly on the stream course with the exception of sample site 40. Copper ranges from 4 ppm to 29 ppm in the James River sediments with no significant increase in metal content at the confluence of streams. Lead values in the sediments range from 10 to 128 ppm for sample sites directly on the James River course. Content in the upper James River remained below 30 ppm Pb. Below the confluences of Pearson, Wilson, and Finley Creeks the lead values in the sediments were consistently higher.

Pearson Creek, a small stream flowing into the James River just east of Springfield, displayed very high Zn, Pb and Cd values, sample sites 38 and 53. Zinc values were 365 ppm and 515 ppm respectively. Lead values were 114 ppm and 389 ppm. Cadmium was 2.7 ppm and 11.6 ppm.

Sample No.	Type	Pb	Cu	Zn	Cd
6	NB	30	0	43	.3
	NS	17	9	34	0
	SS	17	12	43	.3
	SBC	37	9	37	.1
30	EB	49	2	90	1.3
	ES	35	0	83	.3
	WS	42	0	69	.6
	WB	41	1	78	.6
36	EC	113	2	202	1.2
	EB	58	0	81	0
	ES	322	9	415	1.4
	WS	290	8	355	2.1
	WB	258	18	419	2.1
51	EB	562	11	487	3.8
	ES	339	11	464	3.3
	WS	99	2	148	.9
	WB	198	3	378	1.8
53	NB	184	0	547	5.4
	NS	570	6	607	15
	SS	397	11	598	10.7
	SB	355	0	607	13.6
	SC	234	10	350	2.2

[*] For type sample locations see Figure 4. NB-sample from north bank, NS-north stream, SS-south stream SBC-south bank and colluvium, SB-south bank, SC-south side colluvium, EB-east bank, WB-west bank.

Table 2. Heavy metal values (ppm) of stream sediment profiles.[*]

These high values were directly associated with a mineralized fault zone near the sample sites (Fellows, 1970). A sample below an old mine dump on a ridge above sites 38 and 53 on Pearson Creek showed low values in the fine fraction. Resistant primary minerals, sphalerite and galena, were present in the mine dump soil. A stream sediment profile taken on Pearson Creek at site 53 showed high lead values from 184 ppm to 570 ppm, high zinc from 350 ppm to 607 ppm, and high cadmium values from 2.2 ppm to 15 ppm (table 2). Copper was not high. The highest values in the sediment profile occurred on the depositional stream side. A stream sediment profile taken on the James River at site 30 was considerably lower than the Pearson Creek profile (table 2). Lead varied from 35 ppm to 49 ppm, zinc varied from 69 ppm to 90 ppm, copper from 0 to 2 ppm, and cadmium from 0.3 ppm to 1.3 ppm. The higher values noted were from the depositional bank sediments. The average values in the James River (without Wilson, Finley, Flat and Crane Creek samples) for Pb is 76 ppm, Zn - 100 ppm, Cu - 10 ppm and for Cd - 1.4 ppm.

Wilson Creek demonstrated consistently higher heavy metal values throughout its length than the other parts of the basin (refer to figure 6). Highest Pb value of 563 ppm occurs at sample site 45. A decrease in lead occurs downstream from this value with the lowest value of 188 ppm at site 52. The highest Zn content in the fine sediments occurs at site 50 with 380 ppm. This decreases to 257 ppm at site 41, then increases to 337 ppm at sample site 35. Copper was very high and varied from an average of 18 ppm at site 51 to 98 ppm at site 46. Cadmium values were higher in this stream system with values from an average of 1.7 ppm at site 36 to 5.3 ppm at site 50. High metal values occurred both above and below the Springfield sewage treatment plant at site 41. A cross sectional profile taken on upper Wilson Creek, Jordan Creek within Springfield city limits, at site 51 displayed high values with a significant degree of variation (table 2). Lead values for the fine sediment fraction are 99 ppm to 562 ppm in this profile. Zinc varied from 148 ppm to 487 ppm. Cadmium varied from 0.9 ppm to 3.8 ppm. The east bank of the profile site showed the highest metal values, again a depositional feature. A profile of stream sediments was also made at site 36 on Wilson Creek. Lead values were from 58 ppm to 322 ppm. Zinc values ranged from 81 ppm to 419 ppm. Cadmium varied from 0 to 2.1 ppm and Cu varied from 0 to 18 ppm. The depositional side of the channel again had consistently higher metal values.

The average Pb value for all of Wilson Creek is 361 ppm. Zinc averages 272 ppm. The average Cu value is 44 ppm and the average Cd value is 3.0 ppm. These high trace metal values are probably associated with old mine prospects located along Wilson Creek (figures 2 and 6) and fault zones. Industrial and municipal contaminants are present (FWPCA, 1969) and may have been contributors to the higher trace metal values.

Metal contents in Finley Creek fine sediments are considerably less than those in Wilson Creek (figure 7). The average Pb values for these fine sediments is 37 ppm exclusive of site 10 and 85 ppm including site 10. The average zinc values in the fine stream sediments is 39 ppm, exclusive of site 10, and 91 ppm with it. The Cd average is 0.6 ppm without site 10 and 6.2 ppm with it. For Finley Creek, the

Cu average is 6.8 ppm without site 8 and 11.3 ppm with site 8. High zinc values occur at sites 31 with 67 ppm, 13 with 68 ppm, 10 with 610 ppm, and 8 with 117 ppm northeastward upstream. Values at site 10 for Pb, Zn and Cd are erratically high in comparison to the rest of Finley Creek. Cu value of 56 ppm at site 8 is also quite high for Finley Creek. With the exception of site 10 and 13, Pb values are less than 50 ppm. Copper content is below 20 ppm except at site 8. Cadmium content of the fine sediments were low. These ranged from below detection limits to 3.3 ppm at site 8. A high value of 62 ppm occurs at site 10. This is unusually high for this element in these sediments.

A stream sediment profile was taken at site 6. Here the lead values varied from 17 ppm to 37 ppm, zinc from 34 ppm to 43 ppm, Cd from 0 to 0.3 ppm and Cu from 0 to 12 ppm. Values were generally homogeneous at this location with metals in the samples from the depositional side being slightly higher than samples from the erosional side of the channel. High metal values on Finley Creek are probably due to the presence of old mining operations and a mineralized fault zone (figures 2 and 7).

Flat Creek is in the southwest corner of the basin and exhibits low Cu, Pb and Cd values (figure 8). Averages for these metals in the fines are 5 ppm for Cu, 21 ppm for Pb, and 0.8 for Cd. Zinc varies from 12 ppm at site 17 to 376 ppm at site 16. Along the Cassville Anticline sites 14 and 15 showed 110 and 104 ppm Zn, respectively. Higher Pb values also occurred at site 14, but the content is not high compared to Wilson Creek. Site 18 is near a fault and had 106 ppm Zn.

The average zinc value for the fine sediments is 112 ppm. Lead varied in the stream sediments from 15 ppm at site 17 to 34 ppm at site 14. Copper is quite low and varies from 1.5 ppm at site 20 to 10 ppm at 14. Cadmium is also low and varied from 0 to 1.7 ppm. The trace metal variations with respect to geology are illustrated in figure 8.

Crane Creek south of Marionville shows values similar to those of Flat Creek. The Cu average is low at 4 ppm and varies from 0.8 ppm at site 26 and 7 ppm at site 25. Cd averaged 0.6 ppm and ranged from 0.1 ppm at site 27 to 1.0 at site 22. The Pb average in fine stream sediments is 34 ppm with variations from 23 ppm at site 22 to 50 ppm at site 26. Zinc varies from 10 ppm at site 27 to 145 ppm at site 25 and averages 76 ppm. The high Zn value at site 25 is just downstream from the change from Mississippian strata to Ordovician rocks. This change is demonstrated in figure 9. The values on Flat and Crane Creeks are unexpectedly low considering these streams drain a lead mineralized area (McCracken, 1971).

Other stream sediment samples not on any major tributary such as sites 21, 23, and 29, show no high anomalous values of Cu, Pb, Zn or Cd with respect to the basin mean.

THE MEAN AND STANDARD DEVIATIONS

The means and standard deviations calculated for the whole basin are also presented at the end of table 1. The Cu, Pb, and Zn values have standard deviations larger than their respective means. This suggests a high degree of variance exists in the basin samples. A summary of the means and standard deviations for the main streams is

	Element	Std. Dev.	Mean	Above 1 Std. Dev. + Mean	Above 2 Std. Dev. + Mean	No. of Sample Sites
Entire Sampling Group	Cu	20.3	15.5	7	3	52
	Pb	164.6	119.3	8	5	
	Zn	143.7	127.7	10	2	
	Cd	1.33	1.94	7	4	
Wilson Creek	Cu	27.8	44.4	2	0	10
	Pb	164.0	361.3	1	0	
	Zn	92.8	271.6	1	0	
	Cd	1.4	3.0	2	0	
Finley Creek	*Cu (w/o #8)	3.1	6.8	1	1	11
	*Cu (w/ #8)	15.2	11.3	1	1	
	*Pb (w/o #10)	21.9	36.9	2	1	
	*Pb (w/#10)	162.1	85.3	1	1	
	*Zn (w/o #10)	32.2	39.1	1	1	
	*Zn (w/#10)	174.8	91.0	1	1	
	*Cd (w/#10	18.5	6.2	0	0	
	*Cd (w/o #10)	.98	.6	1	0	
James River	Cu	8.0	9.9	2	2	17
	Pb	87.8	75.6	1	1	
	Zn	135.4	99.7	2	2	
	Cd	2.7	1.4	1	1	

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[*] Values w/o #10 noted are different from noted values w/#10
Values w/o #8 noted are different from noted values w/#8

Table 3. Standard deviations and means for James River basin and individual streams.

	Element	Std. Dev.	Mean	Above 1 Std. Dev. + Mean	Above 2 Std. Dev. + Mean	No. of Sample Sites
Flat Creek	Cu	2.6	5.1	1	0	7
	Pb	6.2	21.3	1	1	
	Zn	123.2	111.9	1	1	
	Cd	.56	.8	1	0	
Crane Creek	Cu	2.8	4.1	1	0	5
	Pb	10.7	33.6	0	0	
	Zn	61.2	76.1	1	0	
	Cd	.33	.6	0	0	
Total from Subdivided Basin	Cu			8	4	
	Pb			6	4	
	Zn			7	5	
	Cd			5	1	

TABLE 3. Standard deviations and means for James River basin and individual streams. (continued)

shown below in table 3.

Means and standard deviations were calculated for each major arm in the drainage basin. The results (table 3) show variance within Wilson Creek dropped compared to its mean. This was also noted for other streams with the exception of the more mobile Zn in the James River, Flat Creek, and Finley Creek, including the extremely high values from site 10. Lead is the exception on James River and Finley Creek, including site 10. To obtain exact means and deviations a sample density would be needed which is much greater than that of this reconnaissance survey. At this level, only an inference can be given. Trace metal values distributions in approximate multiples of the basin means are shown for the entire basin.

The number of samples which occur above one standard deviation + the mean of the particular population are cited in table 1 and 3. The number of samples above two standard deviations + the mean are also given. Please note that the number of high values on Wilson Creek masks several values from being seen as "high" in comparison to the rest of the lower values in the basin.

When considered alone, Wilson Creek contains no values above two deviations + mean. With respect to the whole basin, Wilson Creek has several values above one standard deviation + the basin mean. Values higher than one or two standard deviations plus the mean of either the total basin or each tributary are asterisked or double asterisked in table 1. Single asterisked values are considered higher than the normal value for that stream population but not necessarily anomalous. These sites are noted as being worthy of further investigation. A double asterisked value is above the threshold value for anomalous occurrences. A trace metal value that is double asterisked is considered anomalously high for that particular stream population. (Lepeltier, 1969).

MICROSCOPIC STUDY OF MINUS 80 MESH SAMPLES

Microscopic studies were made of the dry minus 80 mesh samples from several locations (Doraibabu, 1973). Samples chosen for this study include those from sites showing typical values, erratically high values and for parts of each profile.

Samples studied consist mainly of quartz grains bonded together in a matrix of organic matter and clay. The quartz grains are rounded to irregular, colorless to brown stained. Chert is also abundant and varies in color. Feldspar occurs in two samples and shows well developed cleavage. Its origin and source are not known. Galena occurs in sample #36 from the west side of the stream and in sample Q in a dry stream channel near an old mine prospect dump. The visible organic material in the sediments consists of black platey, twig-like, and peat-like material. Results of the microscopic study are summarized in table 4 . Symbol explanations are listed at the bottom of the table.

Sample No.	MINERALS AND OTHER MATERIALS							
	Quartz	Chert	Galena	Sphalerite	Clay Material	Organic Matter	Other	Remarks
Q	<.1 mm-.5 mm clear xls, irregular, some grains stained brown	Brownish grayish grains	Metallic-one or two grains, cleavage	Possible grains, small frag. could be chert	Very little clings to organic matter	Blackish, stalk-like material	Feldspar grain	Feldspar may be foreign to sediments
9W	Visible in sediment	Honey colored grains	Absent	Doubtful-none pos. identif.	Very little present	Black-coaly & peaty	-	-
4W	Present, perfect xls visible	Honey colored grains	None visible	Doubtful presence	None noted	Black, twig-like material		higher magnification used
10W	Longer xls fine to coarse	Very little present	None noted	None noted	Very little present	Twig-like organic matter	-	-
49W	Stained grains	Min. quantity	Absent	None pos. identif.	Very little present	Substantial present	Green mineral possibly malachite	

Table 4. Microscopic content of minus 80 mesh fraction of selected stream sediments, James River basin, Missouri (after P. Doraibabu, 1973).

	MINERALS AND OTHER MATERIALS							
Sample No.	Quartz	Chert	Galena	Sphalerite	Clay Material	Organic Matter	Other	Remarks
50W	Coarse to fine, stained brown	Visible	Absent	Not pos. identif.	Flakey, cling to quartz	Black organic material	-	-
51W	Dominant mineral, sharp, angular transparent	larger grains visible	nil	nil	Very little	Black organic matter, sludgy	-	-
51S EB	Very fine grained, clear - some stained	Honey colored	Nil	Nil	Present in very small flakes	Present, black sludgy	-	-
51S ES	Clear & some stained	Present, milky white	Nil	Nil	Very little clay	Black organic matter	Feldspar cleavage frag.	Foreign
52W	Present stained brown	Present	Absent	Possible, opaque, could also be chert	Fine flakes clings to quartz	Present	-	-

Table 4. Microscopic content of minus 80 mesh fraction of selected stream sediments, James River basin, Missouri (after P. Doraibabu, 1973). (continued).

	MINERAL AND OTHER MATERIALS							
Sample No.	Quartz	Chert	Galena	Sphalerite	Clay Material	Organic Matter	Other	Remarks
53W	Clear & brownish	Brownish	Nil	Nil	Very little clay	Black matter	-	-
53W SC	Stained brown	Present, brownish	May be present, very minor	Doubtful presence	Colored, clings to quartz	Black material shows form		
53S SB	Grains fine grained	Pinkish	Nil	Nil	Very little present	Black organic matter	Grains cluster together held by organic matter	
53S SS	Occurs as lumps of aggregated grains	Present, brown, white grains	Nil	Nil	Very little present	Black matter, flakey peaty	-	-
36S WS	Fine to coarse, same as above	Brownish, grayish grains	Metallic 2mm, - non-magnetic, about 3 grains	Possible, honey yellow could be chert	Same as above	Same as above	-	-

Table 4. Microscopic content of minus 80 mesh fraction of selected stream sediments, James River basin, Missouri (after Doraibabu, 1973.) (continued).

Sample No.	MINERAL AND OTHER MATERIALS							
	Quartz	Chert	Galena	Sphalerite	Clay Material	Organic Matter	Other	Remarks
36S ES	Grains angular, some crystals, fine to coarse	Brown & whitish	Nil	Nil	Very little, mixed with organic matter and quartz	Organic matter, peaty - black	Possible feldspar	
30S WS	Fine-grained	Brownish to whitish	May be present in organic matter	Nil	Very little	Black glistening twig-like or bark-like organic matter	Red mineral probably chert.	
30S ES	Larger grains same as above - grains cluster together	Larger grains same as above	Nil	Nil	Very little, difficult to detect	Organic matter present in black, peaty twigs	-	-

#W Sample taken in Winter
#S Sample taken in Spring
#S EB Spring Profile Sample - East Bank
#S ES Spring Profile Sample - East Stream
#S SC Spring Profile - South Colluvium

Table 4. Microscopic content of minus 80 mesh fraction of selected stream sediments, James River basin, Missouri(after P. Doraibabu, 1973). (continued).

STATISTICAL ANALYSIS OF TRACE METAL VALUES IN THE STREAM SEDIMENTS

Statistical analysis is employed here to investigate geologic inferences stated in the previous chapter. For this analysis such inferences are that Wilson Creek's values are unusually high with respect to the rest of the basin and that Finley Creek trace metal values come from a metal environment essentially the same as Flat Creek's.

T-TEST USING PAIRED COORDINATES, BETWEEN WILSON CREEK AND FINLEY CREEK

Student's t-test (Griffiths, 1967) was used as a statistical procedure to determine if a relationship between Cu, Pb, Zn and Cd content of Wilson Creek and Finley Creek exists. Wilson Creek drains an industrialized area of Springfield and is apparently polluted (F.W.P.C.A., 1969). Finley Creek drains a non-industrialized area. The waters are clear and without odor, a real constrast to that of Wilson Creek. Both streams have old mining prospects within their drainage areas. Seven samples were used from each stream for the test and were compared using paired coordinates assuming the comparison was between subdivisions of a whole body. The hypothesis to be considered is: The mean of Wilson Creek and the mean of Finley Creek are two means of random samples from the same normal population. Using this premise, the difference among the means may be stated:

$$\mu_{\bar{x}_{\text{Wilson}} - \bar{x}_{\text{Finley}}} = 0 \quad \text{(Null hypothesis)}$$

The t distribution is used to compare small sets of data. The equation which expresses the t distribution is:

$$t = \frac{(\bar{x} - \mu)\sqrt{n}}{S}$$

where $\bar{x}$ = sample mean
μ = ideal mean
n = no. of samples
S = standard deviation

Using the paired coordinate system, a Finley Creek trace metal value is subtracted from a Wilson Creek value to obtain a value (y_i) representing the difference between the creeks. These differences are then used to calculate a mean ($\bar{y}$) and a standard deviation (Sy). The sample mean and standard deviation are then substituted into the "t" equation with $\mu = 0$. A value for t is derived for n - 1 degrees of freedom. This value is then compared with a theoretical t value at a certain probability level that the difference in means will equal 0. The calculated value will either fall within the confidence limits of the t distribution in which case the means are from the same population or fall outside the specified confidence limit and the null hypothesis would be rejected.

Copper, Pb, and Zn were compared at the 95% and 98% confidence limits. Calculated t values, paired means ($\bar{y}$) and paired standard deviations (Sy's) are listed in table 5. Calculated t values fell well outside the theoretical distributions for Cu, Pb and Zn at the .05 (95%) and .02 (98%) probability levels. This means that stipulated hypothesis is rejected; Cu, Pb, and Zn values of Wilson and Finley Creeks are not random samples from the same population. The calculated t value for Cd is within the theoretical t distribution at both

Assume H_o: $\mu_W = \mu_F$, $\mu_{\overline{x}_W - \overline{x}_F} = 0$

Cu $\sum_{i=1}^{7} y_i = 249.1$ $\overline{y} = 35.6$

$Sy = 42.51$ $\sum_{i=1}^{7} y_i^2 = 19706.7$

$t = 4.85$ with 6 degrees of freedom

$t_{.05,6} = 2.45$ $\therefore \mu_{W_{Cu}} \neq \mu_{F_{Cu}}$

Pb $\sum_{i=1}^{7} y_i = 1718.7$

$\sum y_i^2 = 707400.6$ $\overline{y} = 245.5$

$Sy = 218.1$

$t = 7.87$ with 6 degrees of freedom

$\therefore \mu_{W_{Pb}} \neq \mu_{F_{Pb}}$

Zn $\sum_{i=1}^{7} y_i = 9.51.7$ $\sum y_i^2 = 457728.1$

$\overline{y} = 136$ $Sy = 233.9$

$t = 4.07$ with 6 degrees of freedom

$t_{.02,6} = 3.14$, $t_{.05,6} = 2.45$ $\therefore \mu_{W_{Zn}} \neq \mu_{F_{Zn}}$

Table 5. T-test results between Wilson Creek and Finley Creek.

Cd $\sum_{i=1}^{7} y_i = -47.6$ $\sum y_i^2 = 3458.4$

$\bar{y} = -6.8$ $Sy = 22.9$

$t = -2.1$

$\therefore$ at .05 or .02 probability level

$\mu_{W_{Cd}} = \mu_{F_{Cd}}$

Table 5. T-test results between Wilson Creek and Finley Creek. (continued)

confidence levels. The hypothesis is acceptable, therefore the Cd content distribution could be from the same population.

ANALYSIS OF VARIANCE BETWEEN WILSON CREEK, FINLEY CREEK, AND FLAT CREEK

Comparison of the variance between three streams, Wilson, Finley and Flat Creeks, were next performed using Analysis of Variance (Griffiths, 1967). Again, seven samples from each tributary were incorporated. This method is particularly applicable to a small sample population due to the log-normal distribution found within basin samples. The f distribution used in this test is the theoretical frequency distribution for the ratio of two variances drawn from two populations normally distributed. The postulate used is, there is no significant difference in variances of the Wilson, Finley and Flat Creek populations:

$$\sigma^2_{\text{Wilson}} = \sigma^2_{\text{Finley}} = \sigma^2_{\text{Flat}}.$$

If $F_{\text{calculated}} > F_{\text{theory}}$, the calculated ratio of variances is greater than the theoretical ratio of variances at a specified probability level, the probability that the difference in variances is due to chance alone is small.

For analysis of variance, the variance of a sum of random variables is equal to the sum of the variances of these random variables if the variances are uncorrelated

$$\sum_{i=1}^{n} (x_i - \mu)^2 = \sum_{i=1}^{n} [(x_i - \overline{x}_s) + (\overline{x} - \mu)]^2$$

where x_i = individual value

μ = true mean

$\overline{x}_s$ = sample set mean

The degrees of freedom for the source of variance between populations is J-1, the number of streams used minus one. The degrees of freedom, df, for the source of variance within the population is J(I-1), the number of samples in each stream minus one times the number of streams. The sum of squares (SS) for between is found using

$$\sum_{j=1}^{J} \frac{(\sum_{i=1}^{I} x_{ij})^2}{I} - CT,$$

where

$$CT = \frac{(\sum_{i=1}^{I} \sum_{j=1}^{J} x_{ij})^2}{IJ}$$

$$SS_{within} = \sum_{i=1}^{I} \sum_{j=1}^{J} x_{ij}^2 - \sum_{j=1}^{J} \frac{(x\cdot j)^2}{I}$$

Mean squares (MS) are found by dividing the SS by the respective df. The mean square between (σ^2 experimental + $I\sigma^2 j$) is divided by the mean square within (σ_e^2) to find the value for F which represents the variance between streams. Results are given in table 6.

Copper, Pb, and Zn were found to be greater than the theoretical F value at both the 95% and 98% probability level. The hypothesis,

$$\sigma_W^2 = \sigma_{FIN}^2 = \sigma_{FLAT}^2$$

Cu

Source	df	SS	MS	F	$F_{0.5,3,18}$
Between	2	16629.1	8314.6	18.07	3.55
Within	18	8282.9	460.2		$F_{.025,2,18}$
Total	20				4.56

Pb

Source	df	SS	MS	F
Between	2	944966	472033	83.3
Within	18	102050	5669	
Total	20			

Zn

Source	df	SS	MS	F
Between	2	615615	307808	12.5
Within	18	442599	24589	
Total	20			

Cd

Source	df	SS	MS	F
Between	2	509.2	254.6	1.43
Within	18	3208	178.2	
Total	20			

Table 6. Results of analysis of variance between Wilson, Finley, and Flat Creeks.

is not valid. This implies that these metals were taken from more than one population. Cd fell within both theoretical F values indicating that it could be from the same population.

T-TEST USING MEANS AND STANDARD DEVIATIONS BETWEEN WILSON CREEK AND FINLEY CREEK, AND BETWEEN FINLEY CREEK AND FLAT CREEK

Because the results of the t-test with paired coordinates and the analysis of variance suggests that the means are significantly different and that the random samples are independently made from each other, a second t test was performed. This compares Wilson Creek with Finley Creek and Finley Creek with Flat Creek using comparison of the means and standard deviations in table 3. The equation used to calculate the t distribution is:

$$t = \frac{\bar{x}_{\text{Wilson}} - \bar{x}_{\text{Finley}}}{\sqrt{\frac{S_W^2}{n_F} + \frac{S_F^2}{n_W}}\ \sqrt{\frac{n_W + n_F}{n_W + n_F}}\ -2}$$

where S^2 = variance of stream

$\bar{x}$ = sample mean

n = number of samples considered for this test in a stream

The null hypothesis assumed was:

$$\mu_{\bar{x}_{\text{Wilson}} - \bar{x}_{\text{Finley}}} = 0 \text{ and } \mu_{\bar{x}_{\text{Finley}} - \bar{x}_{\text{Flat}}} = 0.$$

With this method the number of degrees of freedom is found by $n_1 + n_2 - 2$. The results of this testing is in included in table 7. In the Wilson and Finley test, the results were similar to the first t-test. Cu, Pb, and Zn exceeded the theoretical t value at both the .05 and .02 levels. This again implies these values were drawn from different populations. Cd remained within the theoretical t values.

Wilson Creek and Finley Creek

$$H_o: \mu_{\overline{x}_{WILSON}} - \mu_{\overline{x}_{FINLEY}} = 0$$

$$df = n_1 + n_2 - 2$$

Cu t = 3.98 w/df = 18

Pb t = 5.87, df = 18

Zn t = 7.11, df = 18

Cd t = 4.2, df = 18

Finley Creek and Flat Creek

$$H_o: \overline{x}_{FINLEY} - \overline{x}_{FLAT} = 0$$

Cu t = 1.27, w/df = 15

Pb t = 1.77, df = 15

Zn t = -1.67, df = 15

Cd t = -.33, df = 15

Table 7. T-test using means and standard deviations coordinates.

The Finley and Flat test showed that Cu, Pb, Zn and Cd were within the theoretical t distribution. The null hypothesis is valid, there is no significant difference in the means. This implies that the trace metal values of Finley Creek and Flat Creek are taken from the same population.

Because the lab technique was the same for all sample preparations, any variation due to this process could be considered systematic. Analytical variance was partially reduced by subtracting the trace metal values of a blank prepared with each sample set from the values obtained in that sample set. The blank solution gives a reasonable lower limit for the detection of trace metals in the sample solutions. The major source of variance must be some characteristic(s) within the basin or sampling procedure.

There are two types of variance to be considered. One, within sampling sites, i.e. two or more samples at the same site giving non-identical results, and the variance between sample sites. Variations between sites are the differences in geologic and geochemical character of the differing sediment sample locations. For this study, variations are dependent on the proximity of the sample to a lithologic or structural change, the proximity of the sample to old mine prospects and other areas of mineralization, and contributions from outside sources geographically controlled.

It was thought that record changes in water levels in the streams, forcing sampling to be made at irregular points in the stream channel, would cause a great deal of variation in the trace metal values. The stream profiles disprove this, showing that for a particular sample location, e.g. 6, 30, etc, the cross section values remain relatively homogeneous for each element. The increased water volume in the winter and spring made recovery of the fines difficult. This did not result in a significant variance. However, the distance the sediment traveled, or how far from the source the sediment is, is a major source of variation and would be part of the variation between sites. Some of the very high metal values may be caused by the addition of galena cleavage fragments in the sample.

The main differences in trace metal value must be caused by changes in the geochemical environment between sample locations. This was demonstrated by geologic reasoning in the Geochemical Results section and reinforced in this section by use of statistics on small sampling sets.

SUMMARY AND CONCLUSIONS

The James River basin has several mineralized areas where sphalerite and galena fill fractures in fault zones. Cadmium, probably included in the mineral greenockite, is associated with these deposits (Shepard, 1908). Cadmium may also occur within the sphalerite lattice (Guild, 1967). High Cd values are directly associated with high zinc values.

Highest metal values occur on Wilson Creek, Pearson Creek, upper Flat Creek and middle Finley Creek near zones of faulting, mineralization and in or about areas of industrial activity. Lead values range from 10 ppm to 593 ppm in the fine sediment fraction. Zinc behaves similarly and ranges from below detection limits to 610 ppm. High copper values in the fine stream sediments occur on Wilson Creek and at one location on upper Finley Creek. Cadmium remains relatively constant in the basin with ranges from below detection limits to 5 ppm. Two cadmium values occur above this. One is on Pearson Creek and another on middle Finley Creek. Both highs occur near known mineralized zones.

Wilson Creek is polluted with various forms of organic and non-metal compounds (F.W.P.C.A., 1969, Griswald, personal communication, 1973). High heavy trace metal values exist in the fine sediments throughout the length of this creek. The major heavy metal sources are probably the old mining prospects on Wilson Creek with other possible sources being industrial contaminants, street run off, and waste disposal. No conclusive evidence exists in this study to link heavy trace metal values in the sediments with the Springfield liquid waste disposal plant on Wilson Creek near site 41. Other outside sources such as random dumping of contaminants, old car bodies, etc. are other possibilities for metal sources on Wilson Creek as well as throughout the basin, but to date these cannot be directly correlated to the heavy metal values obtained at the sample sites.

Pearson Creek's higher values at sites 38 and 53 are directly related to a mineralized fault and to old prospect pits. Heavy metal values in James River sediments are relatively consistent. High copper values do occur at sites 28 and 40. The former values may be related to faulting and mineralization. The higher values at site 40 may be related to a railroad line which parallels the James River in this area.

Heavy metal values on Finley Creek are low with the exception of site 10. Here, the waters drain an area containing an old mining prospect and the metal content in the fine sediment rises. On Finley Creek at site 8 high Cu, Zn and Cd may be related to known mineralization along a fault. Unusually high Cu and Pb values for Finley Creek occur at site 13 and these may also be related to mineralized faults parallel to those shown in figures 2 and 7.

Crane Creek fine sediments have rather low heavy metal values in comparison with the rest of the basin. A high value for Crane Creek does occur at site 25 in Cu and Zn. Flat Creek is also low in heavy metal content. Higher Cu and Pb, however, do occur at site 14, but are considered abnormal for this stream. Rather high Zn values occur at site 16. This may be attributed to nearby mineralization (Kisvarsanyi, 1965). The mineralization did not cause the values to be high along the full course of both creeks.

A sample taken from a dry creek bed near an old mining dump containing clays and small sphalerite and galena fragments showed low values. Galena and sphalerite were also found in another sample. Some metal may have been coprecipitated by Fe or Mn oxides which coat quartz and chert grains or form veinlets in minute cracks within the grains. Some of these coprecipitated metals could be released in the hot nitric acid leach analysis. Trace metals may also have been absorbed onto the finer clay and organic matter. The exact source of the heavy metal values in the minus 80 mesh fraction is not known.

Results for each metal in ppm for the stream cross-sectional profiles at the different sample sites are summarized in table 2 and sampling at a profile are illustrated by figure 4. There is an apparent preference in higher metal profile values for stream sediments taken from the depositional side of a channel versus the erosional side. Flood plain and colluvium metal values are less than those in the active channel sediments. These data suggest that at a location of higher metal content, e.g. at site 51, the metal values in the profile remain high. In low metal content locations, e.g. site 6, metal values in the profile remain low.

Individual streams were considered separately to determine average values for each drainage area and then examined for the amount of individual variance. Standard deviations for the whole basin of Cu, Pb and Zn were higher than their means displaying the high degree of variability in trace metal value within the river basin sediments. The standard deviations of the individual groupings dropped below their mean with the exception of Zn on the James River, Finley, Flat and Crane Creeks and Pb on the James River. Trace metal values were consistently higher on Wilson Creek and many were not considered anomalous with respect to the Wilson Creek population. These values were definitely high in reference to the rest of the basin population. Several sample sites have trace metal values more than two standard deviations implying anomalous values (Lepeltier, 1969).

Three t tests and an analysis of variance test were made on the data. These suggest that the basin represents two or more separate populations for the heavy metals. The significant differences in means and variations indicate a number of uncontrollable or unaccountable variables have entered the data. This may partly be explained by the occurrence of mineralization at random locations in an area that should be, by lithology, a metal poor area. Using these statistical methods, variations in cadmium values were not found to be significantly high. This is partially due to the low availability of the element. Repeated sampling indicates a fair degree of reproducibility in results and stream sediment profiles have fair homogeneity in metal distributions.

This reconnaissance study of Cu, Pb, Zn and Cd in fine fraction sediments of the James River basin indicates they exist in the stream sediments in amounts higher than average for carbonate rocks elsewhere. Lead in the form of galena and zinc as sphalerite are present in the sediments. High metal values are principally related to mineralization in faults of the area and to old mining prospects and former operations. Transportation of the fine-grained sediment from such metal sources is the main control for heavy metal content in the random sediment samples obtained. More detailed sampling and analyses would yield more exact locations of metal sources and permit a better statistical analysis of metal populations throughout the basin.

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APPENDIX I

SEDIMENT SAMPLE LOCATIONS AND AVERAGE ANNUAL pH FOR 1973

Site No.	Location	pH
1	29N-19W-17-bb	7.6
2	29N-19W-8-ac	7.5
3	29N-18W-6-ac	7.3
4	29N-18W-5-ab	7.6
5	29N-18W-12-ad	7.0
6	29N-18W-23-ca	7.2
7	28N-18W-23-bd	7.3
8	28N-18W-24-cb	7.3
9	27N-19W-12-ba	7.1
10	27N-19W-1-ca	7.2
11	27N-19W-18-db	7.7
12	27N-20W-18-cb	7.9
13	26N-22W-1-bd	7.9
14	23N-27W-3-cd	7.0
15	24N-27W-12-ca	8.0
16	24N-27W-1-ab	7.5
17	24N-26W-24-aa	7.6
18	24N-26W-24-ad	7.9
19	23N-25W-6-ca	7.8
20	24N-24W-30-da	8.1
21	24N-24W-17-dc	7.6
22	26N-24W-29-cd	7.7
23	23N-23W-17-db	8.2
24	24N-23W-7-cb	7.7
25	25N-24W-1-cd	7.6
26	25N-23W-6-ab	8.0
27	25N-23W-9-dc	7.9
28	25N-23W-1-aa	8.2

APPENDIX I

SEDIMENT SAMPLE LOCATIONS AND AVERAGE ANNUAL pH FOR 1973

Site No.	Location	pH
29	25N-23W-12-da	7.2
30	26N-22W-8-dc	7.8
31	26N-22W-8-dd	7.7
32	27N-22W-32-ab	7.8
33	27N-22W-5-bc	7.7
34	28N-23W-35-cd	7.7
35	28N-23W-25-cb	7.4
36	28N-23W-24-bc	7.0
37	29N-20W-31-bb	7.9
38	29N-21W-35-ab	7.4
39	28N-21W-15-cc	7.5
40	28N-21W-30-ac	7.4
41	29N-22W-7-aa	7.3
43	24N-23W-7-ca	7.7
44	26N-24W-29-cc	7.5
45	29N-22W-27-cb	7.5
46	29N-22W-29-cb	7.0
47	28N-17W-7-ba	7.8
48	28N-17W-20-dd	7.6
49	29N-22W-26-cc	7.6
50	29N-22W-23-bc	7.4
51	29N-22W-27-db	7.2
52	29N-22W-28-bb	6.8
53	29N-21W-35-ac	7.9