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HEAVY METALS IN THE MAIN STREAMS

OF THE

JAMES RIVER BASIN, MISSOURI

by

RICHARD JEROME LANCE, 1946-

# A THESIS

Presented to the Faculty of the Graduate School of the

UNIVERSITY OF MISSOURI-ROLLA

In Partial Fulfillment of the Requirements for the Degree

MASTER OF SCIENCE IN GEOLOGY

1973

Approved by Approved by Approved by Approved by C.1 Approved by C.1 Approved by C.1

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# PUBLICATION THESIS OPTION

This thesis has been prepared in the style utilized by the Missouri Geological Survey and Water Resources, Water Resource Reports. This thesis, when combined with other related theses, will be presented for publication by the Missouri Geological Survey. The title page, publication thesis option page, and vita have been added for purposes normal to thesis writing.

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# HEAVY METALS IN THE MAIN STREAMS OF THE JAMES RIVER BASIN, MISSOURI

Richard J. Lance

# ABSTRACT

Demands on water resources in the James River basin have greatly increased. Industrial plants and lead-zinc prospects in the basin are potential sources of heavy metal additions to the waters of the area. The study determines the heavy metal content and distribution in the streams of the basin.

Approximately 50 water samples were collected each season and analyzed by atomic absorption techniques. Field determinations of temperature, specific conductance, pH, and effective alkalinity were also made.

Ranges of heavy metal content were: (1) mercury - <0.1 to 0.3 ppb (summer only); (2) zinc - <1 to 80 ppb; (3) copper - <1 to 18 ppb; (4) lead - <1 to 41 ppb; (5) cadmium - <1 to 7 ppb; and (6) iron -<50 to 277 ppb.

The urban areas of Springfield contribute dissolved heavy metals to the surface streams. The Southwest Springfield Sewage Treatment Plant is not a significant source.

Seasonal and geographic variations were apparent. Geo-hydrologic contributions appear to be related to mineralized and faulted areas. Variation at individual sample sites is not considered of great significance. Filtered water samples meet PHS heavy metal standards for public drinking water.

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#### INTRODUCTION

# PURPOSE AND SCOPE

The presence of many old lead-zinc mines and prospects in southwestern Missouri has raised concern that ground and surface waters may have received additions of heavy metals from these mineralized areas. The scenic beauty of this area and the resultant extensive tourism has generated public interest in the quality of the waters available for domestic, industrial, and recreational uses. Plant or animal life in contact with streams having high metal concentrations may be adversely affected by these metals and become a part of the food chain for the region. Hence, knowledge of type and amount of dissolved heavy metals in the waters of an area is essential in the evaluation of any water source.

This study was initiated to determine the dissolved heavy metal content of the ground and surface waters in the James River basin and to evaluate possible sources for these metals.

The James River basin of southwestern Missouri lies on the fringe of the intensely mineralized Tri-State zinc mining district. Within the basin itself are several small mineralized areas.

Springfield, the third most populous city of the state, is on the northern edge of the basin. The presence of this major city offered an opportunity to compare and contrast natural heavy metal additions with those which might have been contributed by an industrialized and densely populated area. The original purpose of the study was to collect water samples from selected streams, springs and water wells within the James River basin and analyze these samples for the heavy metals - mercury, zinc, copper, lead, cadmium, and iron. Patterns of heavy metal distributions were to be correlated as nearly as possible with geo-hydrologic units, mineralized areas, geologic structures, or industrial and population centers.

Another aspect of the project concerned the possible determination of the minimum number of water samples which could give an adequate representation of the heavy metal content of surface waters in similar environments. Availability of such information could improve other similar future studies.

To accomplish the proposed goals, a research project of broad scope was planned. The extensive program was to consist of approximately 150 samples collected each season of the year for determinations of geographic and seasonal variations. Because time and financial resources did not permit such intensive sampling, the project was modified to a more general reconnaissance study relating only to surface water. The original objectives on surface waters were essentially fulfilled by this study. About 50 water samples were collected from selected streams during three distinct seasons of the year. These samples were analyzed in the geochemistry laboratory at the University of Missouri-Rolla, Rolla, Missouri.

Each water sample was analyzed on a Perkin-Elmer Model 303 atomic absorption spectrophotometer. Determinations were made for lead, zinc, copper, and iron content. These heavy metals are common to the nearby

Tri-State mining district. Cadmium and mercury, though much less common in waters, are more toxic and are known to be associated with mineralization in the district. These metals were also included in the analytical program.

## ACKNOWLEDGEMENTS

Dr. Paul Dean Proctor supervised the research and gave valuable guidance to the writing of this thesis.

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I greatly appreciate the assistance of Anita Williams and William Head in the gathering of data. Appreciation also goes to the Missouri Geological Survey and Water Resources for the use of their vehicle during a portion of the field work. The Missouri Geological Survey staff gave help and support to this thesis.

I must also acknowledge the understanding of my wife, Margaret, and daughter, Becky, during the days, nights, and weekends of field and laboratory work.

## PREVIOUS WORK

In the late eighteen hundreds, Shepard (1898) conducted a rather comprehensive study of the geology and mineral occurences of Greene County and portions of the surrounding counties. Since that time, Missouri Geological Survey personnel have studied the stratigraphy and revised the stratigraphic nomenclature as used by Shepard (Clark and Beveridge, 1952).

Two of the most pertinent references for the stratigraphy of the James River basin are the report, <u>The Stratigraphic Succession in</u> <u>Missouri</u> (Howe, 1971), and the guidebook prepared by Vineyard and Fellows (1967).

A report on water resources in the Joplin, Missouri area (Feder, <u>et al</u>., 1969) deals with an area of similar geologic and hydrologic characteristics. In the Joplin report the only heavy metals listed were zinc and sometimes iron and copper.

In Springfield, Missouri, effluent from industrialization and urban growth has generated a great deal of concern for the present and future quality of surface waters in the James River basin. After several fish kills had occurred in the James River, an intensive study was made to determine the pollution contributions of the Southwest Springfield Sewage Treatment Plant and the industries in the Wilson Creek area of western Springfield (Harvey and Skelton, 1968; and F.W.P.C.A., 1969). This study did not include any heavy metals in the analytical program.

Miesch, <u>et al</u>. (1970) conducted a reconnaissance geochemical survey of Missouri. This study gives a general view of the trace elements and heavy metal distributions in the water, sediments, soils, and plants. No water samples were taken in the James River basin.

The Missouri Clean Water Commission (C. S. Decker, Personal Communication, 1973) has been monitoring the heavy metals in the streams

of southwestern Missouri. The City of Springfield, Office of Industrial Waste Surveillance and Enforcement monitors waste discharges from the city's industries (H. Criswell, personal communication, 1973).

Proctor, <u>et al</u>. (1973) conducted an investigation very similar to the present one. The major difference lies in the geographic restriction in the earlier study to the urban areas of Joplin and Springfield, Missouri. Heavy metals in the ground and surface waters were investigated.

Head (1973) recently completed a companion reconnaissance project. He investigated concentrations of cadmium, zinc, copper, and lead in the fine sediments of the James River basin.

## AREA OF STUDY

### LOCATION AND ACCESSIBILITY

The James River basin includes portions of Barry, Stone, Lawrence, Christian, Greene, Douglas and Webster counties in southwestern Missouri. The basin is accessible by several major highways -Interstate 44 is on the northern boundary. U.S. Highway 65 runs northsouth from Springfield to Branson and approximately divides the basin. U.S. Highway 60 runs in an east-west direction from Springfield to the eastern boundary of the basin near the town of Seymour.

Most of the non-hard surface county roads are in good condition. Travel on them offers good access and excellent scenic beauty. Occasional high water conditions in the area makes crossing of some low-water bridges impossible.

#### PHYSIOGRAPHIC FEATURES

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The James River drains an area of approximately 1460 square miles. It is the largest tributary to the White River in Missouri. The river basin approximates 60 miles in length and is about 20 miles wide in the upper two-thirds and 30 miles wide in the lower third of its length. The basin is predominantly in the Springfield Plateau physiographic province. However, a small portion of the upper reaches of both James River and Finley Creek and also the southern one-fourth of the basin are in the Ozark Mountains. Elevation in the basin varies from approximately 1675 feet above sea level near Seymour to slightly less than 1000 feet in the areas flooded by Table Rock Lake.

James River has four major tributaries: Wilson, Finley, Flat, and Crane Creeks. Wilson Creek begins within the Springfield limits and is utilized to dilute treated effluents from the municipal sewage treatment plant located southwest of the city. The creek then flows southward through the Wilson Creek Battlefield National Park and into the James River approximately 9 miles southwest of Springfield. Volume of flow in Wilson Creek is partly regulated by the amount of sewage effluent. Finley Creek drains the largest tributary area. This creek flows westward from near Seymour and drains the southeastern sections of the basin. It joins the James River in the northeastern corner of Stone County. Flat Creek, in the southwestern part of the area, originally flowed from near Cassville, Missouri, through its basin and into James River near Cape Fair. Because of the addition of Table Rock Reservoir, it now flows directly into this lake about 5 miles northwest

of Cape Fair. Crane Creek rises near Aurora and flows southeastward joining James River near the town of Hurley.

# CLIMATE

The James River basin lies within the continental climatic regime of central North America. Annual precipitation ranges from 40 to 44 inches. Average annual runoff in the area is 12 to 14 inches. Summers are hot and often dry, with most of the precipitation occuring as violent thundershowers of short duration. Fall and early winter are normally dry and rather pleasant. Snowfall occurs most frequently from December through February; although, some snowfalls may occur in November and March. Spring and early summer seasons are warm and often very wet. The average annual temperature is approximately 14 degrees centigrade (57°F).

## CULTURE

Population of the James River basin has increased significantly during the decade 1960-70 (U.S. Bureau of Census, 1970). Of the population centers with 1000 persons or more, twelve within the basin and eight centers on the basin perimeter have had population changes ranging from (-)12.5 percent to (+)73.3 percent. The average change was approximately (+)28 percent. Springfield (120,000 population) is the third largest city in the state and is the largest population and industrial center in the basin. It has had a population increase of approximately 25 percent during the decade. The growth in population has resulted in a much greater demand for usage of the water resources in the basin. Other than at Springfield, there is very little manufacturing industry within the basin. Forestry, dairy farming, cattle raising, and truck farming are widely practiced throughout the area.

Two significant man-made lakes lie within the basin. These affect the waters in the area. Lake Springfield, just south of the city, was completed in 1956. These lake waters are used for cooling of the condensers in the steam driven turbine generators. These generators provide electricity and the lake waters provide recreation for the inhabitants of Springfield.

Table Rock Dam, on the White River, was completed in 1958. This reservoir controls floods, generates hydroelectric power, and provides a major recreational area for the state and surrounding areas. The lower reaches of the James River, below Galena, Missouri, are flooded by the waters of Table Rock Lake. The lake is famous for the catches of large white bass and other game fish.

#### GEOLOGIC SETTING

Most of the rocks exposed in and around the James River basin are of marine origin. These rocks were formed some 450 million to 325 million years ago and comprise parts of the Ordovician, Devonian, Mississippian, and Pennsylvanian Systems of the Paleozoic Era.

Primary sources for the following stratigraphic discussions are <u>The Stratigraphic Succession of Missouri</u> (Howe, 1961); the guidebook by Vineyard and Fellows (1967); the structural geology report by Mary McCracken (1971); and a report by Shepard (1898) concerned mineralization. A generalized geologic map and a generalized stratigraphic column for the units in the James River basin was compiled by Head (1973) and the author and are shown in Figures 1 and 2.

# STRATIGRAPHY

# ORDOVICIAN SYSTEM

The Ordovician System is made up of rocks of the Canadian, Champlainian, and Cincinnatian Series. These lie around the flanks of the Ozark dome and dip gently away from the central portion. In the James River basin, only units from the Canadian Series are exposed. The Ordovician System is separated from other systems by conspicuous unconformities at its base and top.

#### Canadian Series

The Canadian Series is composed of the Gasconade, Roubidoux, Jefferson City, Cotter, Powell, and Smithville formations. Only the Jefferson City-Cotter formation (undifferentiated) is exposed in the



Figure 1: Generalized geologic map of James River basin, Missouri showing mineralized areas (compiled by W. J. Head and R. J. Lance, 1973).

SYSTEM	SERIES	FORMATION	LITHOLOGY
PENN.	DESMOIN- ESIAN	CHEROKEE GROUP	
	CHESTER- IAN	CARTERVILLE FORMATION	
IAN	MERAMEC- IAN	WARSAW FORMATION	0
SSIPP	AN	BURLINGTON / KEOKUK LIMESTONE	
SSI	AGE	ELSEY FORMATION	00
IW	SO	PIERSON / REEDS SPRING FORMATION	
	KINDER- HOOKIAN	NORTHVIEW / COMPTON FORMATION	
ORDOVICIAN	CANADIAN	COTTER DOLOMITE	- 77 
		JEFFERSON CITY DOLOMITE	
		ROUBIDOUX FORMATION	
		GASCONADE DOLOMITE	0  

Figure 2: Stratigraphic section of James River basin. Exposures mainly include units above the Roubidoux Formation.

James River basin.

Jefferson City-Cotter Formation (undifferentiated) - The Jefferson City formation and the Cotter formation are commonly lumped together due to the difficulty of separation on the basis of insoluble residues (Grohskopf and McCracken, 1949).

The aggregate formation is composed of approximately 180 feet of brown, finely crystalline dolomites with some chert and sandstone. The formation gradually thickens toward the southwest. The included white chert often contains molds and casts of gastropods. Some moundlike algal structures are also present in the formation. Locally, sphalerite-filled vugs have been observed.

Large springs and caverns often occur in this dolomite section.

## SILURIAN SYSTEM

Because of a regional unconformity and related erosion, rocks of the Silurian System are not present in the James River basin.

#### DEVONIAN SYSTEM

The Devonian System is represented by the Chattanooga shale (L. D. Fellows, personal communication, 1973; T. R. Beveridge, personal communication, 1973). Chattanooga Formation - This is a fissile, black, carbonaceous, slightly arenaceous, spore-bearing shale with local concentrations of pyrite nodules and concretions. The formation is 10-12 feet thick in Barry County. It thins toward the northeast until only scattered occurences are known in Greene and Christian Counties. The shale unconformably overlies Ordovician dolomites and is unconformably overlain by various Mississippian formations.

### MISSISSIPPIAN SYSTEM

The Mississippian System is composed of the Kinderhookian, Osagean, Meramecian, and Chesterian Series. These series are separated by hardly noticable unconformities, but by definite fossil breaks. The lithology variations from lateral facies changes complicates the stratigraphy. This system is unconformably overlain by Pennsylvanian strata.

# Kinderhookian Series

The Kinderhookian Series is represented in the area by the Bachelor, Compton, and Northview formations.

Bachelor Formation - The basal unit of the Kinderhookian Series is a thin, 5-18 inches, but persistent green sandstone and shale.

Compton Formation - This formation overlies the Bachelor formation and consists of grayish-green, thin-bedded, crinoidal limestones approximately 12-14 feet thick. It is locally dolomitic and contains some chert.

Northview Formation - This formation is above the Compton and is the upper unit of the Kinderhookian Series. It is generally thin, 2-5 feet thick, bluish-green siltstone and shale. In the type area of Greene and Webster Counties, the Northview reaches a maximum thickness of 80 feet. From this thickness it thins to the southwest. The Northview exhibits characteristic recessive weathering in both surface and cavern exposures. Where exposed, the formation appears to be conformable with the overlying Pierson formation.

### Osagean Series

The Osagean Series is the most complete rock sequence in southwest

Missouri. It is composed of very similar cherty limestones that have an aggregate thickness of about 250 feet. The Pierson, Reeds Spring, Elsey, Burlington, and Keokuk formations make up the Series.

Pierson Formation - This formation consists of grayish-brown crinoidal limestone that has some chert in the upper portion. The unit is approximately 35-40 feet thick in the Greene County type area. It thickens southward from Greene County.

Reeds Spring Formation - The formation is a medium gray, finely crystalline limestone with irregular beds and nodules of bluish chert. The chert is very abundant, ranging from 30-60 percent of the formation. The Reeds Spring is known in the basin only as far north as Ozark, Missouri. In this area it is about 50-60 feet thick. The Reeds Spring conformably overlies the Pierson formation.

Elsey Formation - This unit is medium-gray, finely crystalline limestone with large smooth nodules and discontinuous beds of chert. The chert nodules are flattened parallel to the bedding plane. The formation is about 30 feet thick in the Springfield area and gradually thickens to the southwest.

Burlington-Keokuk Formation - The Burlington and the over-lying Keokuk limestones are so similar in appearance in this area that they are commonly grouped together. The formation is composed of light gray, medium to thick-bedded, very crinoidal limestone containing scattered chert nodules.

The Springfield Plateau is largely capped with about 160 feet of this limestone formation. The Warsaw formation of the Meramecian Series when it is present, conformably overlies the Burlington-Keokuk

formation.

## Meramecian Series

Only the Warsaw formation of the Meramecian Series is present in this part of the state. The many lithologic similarities between the Meramecian and Osagean Series create an obscure boundary between the two series.

Warsaw Formation - This unit is the basal member of the Meramecian Series. It is a slightly cherty limestone and is very similar to the Keokuk formation. In this area the Warsaw is 60-185 feet thick. <u>Chesterian</u> Series

The Chesterian Series unconformably overlies the Meramecian Series. Rocks of this series are present only in the extreme southwestern corner of the basin in Barry County. These are an outlier of extensive formations found in Arkansas and northeastern Oklahoma. This series is composed of the Hindsville, Batesville, and Fayetteville formations and does not exceed 120 feet thickness in the James River basin. PENNSYLVANIAN SYSTEM

The Pennsylvanian System is of very patchy distribution in southwestern Missouri. It is present on the western perimeter of the James River basin as sandstone-siltstone outliers of the Krebs subgroup of the Cherokee group in the Desmoinesian Series.

# RESIDUUM

The red clay and chert residuum in the area is composed of the least soluble constituents of the original rocks. Thickness of the residuum is highly variable and may be as much as 60 feet.

Exposed limestones in the area weather with a highly irregular

contact of bedrock and residuum that appears pinnacled. These pinnacles cause problems in foundation construction of large buildings (P. D. Proctor, Personal Communication, 1972).

# STRUCTURE

Only a very small portion of the James River basin has been geologically mapped (Clark, 1941; Fellows, 1970; Beveridge, 1970). Reconnaissance geologic mapping by members of the Missouri Geological Survey has indicated the presence of a few anticlinal structures and several faults (McCracken, 1971).

Most of the known structures trend westerly to northwesterly (see Figure 1). Displacements along faults are approximately 50-60 feet with a maximum of 140 feet displacement on the Diggins fault near Seymour in Webster County.

In southwestern Barry County the Greasy Creek fault trends northeast and has a vertical displacement of about 250 feet. This relatively large displacement is responsible for the preservation of the Hindsville and Batesville Formations of the Chesterian Series, uppermost units of the Mississippian System.

#### BASE METAL MINERALIZATION

In the James River basin, base metal sulfide mineralization occurs mainly in the Mississippian strata (Shepard, 1898). Most of the economic mineralization occurred in what Shepard (1898) described as the Upper Burlington Formation and the Hannibal shale - or, the present Burlington-Keokuk and the Northview formations. These formations are apparently more susceptible to replacement than are the other units of the Mississippian System. Figure 1 illustrates the distribution of areas with known mineralization.

Sulfide deposition in this area, as in parts of the Joplin area (Feder, <u>et al.</u>, 1969), was intimately associated with breccias along fault zones and solution features.

# STREAMFLOW IN RELATION TO GEOLOGIC SETTING

Surface and underground drainage are governed by many common factors. Some of these are: faults, joints, folds, and solubility of the bedrock. Surface streams, especially, readily follow these structural features.

The Springfield Plateau, capped by Burlington-Keokuk limestone, is a karst area. Infiltrating rainwater has dissolved away some of the limestone forming solution channels and caverns. Some of these caverns have collapsed and formed sinkholes. In many areas, solution activity is also evident along bedding planes, lithologic changes, joints, and faults.

Locating sewage lagoons, lakes, and other pollutant holding ponds in karstic areas creates a potential danger for ground-water pollution. When the groundwater becomes polluted, surface water may also be affected. Harvey and Skelton (1968), through seismic and dye tracing studies, demonstrated the intimate interrelationship of surface and underground drainage in connection with effluent dispersion from the Southwest Springfield Sewage Treatment Plant.

As noted, knowledge of groundwater movement is important. The

quality of water in the area streams may be directly related to the quality of the groundwaters as the streams are largely spring fed.

As shown in Figure 1, the headwaters of the James River and Finley Creek flow for approximately 25 miles across Ordovician formations. These streams then flow over Mississippian strata, until about 5 miles below the mouth of Wilson Creek where the river once again flows over Ordovician rocks. It is unclear whether this change is the result of an unrecognized synclinal structure, faulting or a reflection of the variation of thickness in the Mississippian System. Possibly a combination of these factors is involved.

## METHOD OF INVESTIGATION

As standardization of sample collection and analysis was desired, the field collection and analytical methods of Brown, <u>et al</u>. (1970) were followed with minor modification.

# SAMPLE SITE SELECTION

Preliminary sample sites were selected using accessibility, uniformity of coverage, and proximity to established stream gaging stations as criteria. The importance of easily accessible, yet fairly representative, sample locations is evident when one considers the areal extent of the James River basin and the fact that most of the county roads are not hard surfaced. The uniformity of coverage is desirable in order to properly relate geologic and hydrologic conditions to analytical results.

Three active stream gaging, water-quality stations are maintained in the James River basin by the United States Geological Survey (U.S. Geological Survey, 1971). These station sites were included in the present study to facilitate comparison of water data. These stations supply data on seasonal change in stream-flow conditions and may permit interpretation of the effects of dilution or concentration on heavy metal values.

Uniform coverage in a surface water sampling program that covers about 1500 square miles is difficult. The presence of Springfield required a much higher water sample density to more adequately outline possible areas of heavy metal additions from the more densely populated and industrialized areas (Figure 3).

The unexpected problem of some selected sample sites being dry resulted from an extremely dry period experienced in July and early August, 1972. Most of these dry streams were later sampled during high water conditions of the winter and spring collection periods of 1972-73.

### SAMPLING PROCEDURES

To obtain a homogeneous sample, the water sample was generally collected from that portion of the stream having swift turbulent water (Figure 4). In all cases to minimize contamination, this collection was made upstream from the highway or county road bridge. Immediately after collection, a one liter portion was filtered through a 0.45 micron membrane filter (Figure 5) and placed in an acid cleaned polyethlene bottle. This filtrate was acidified (Figure 6) with approximately 10 milliters of reagent grade 1:1 nitric acid. The sample bottle was tightly capped until time of analysis. Filtration was effected to obtain water with only dissolved heavy metals for analysis. The acidification of the sample to a pH of about 3.0 minimized oxidation, precipitation, and adsorption of the metals on the walls of the sample container.

#### FIELD TESTS

Several physical measurements were made in the field using a fresh unfiltered portion of the sample. These included: (a) Temperature of water in degrees centigrade; (b) pH - measured by a battery operated



Figure 3: Location map of main stream sample sites, James River basin, Missouri.



Figure 4. Typical sample site - Flat Creek. Sample taken from turbulent water zone.



Figure 5: Field filtration of sample using the Skougstad filter assembly.



Figure 6: Sample acidification for retention of dissolved metals until analysis.



Figure 7: Field measurement - pH of unfiltered sample.

Sargent-Welch Model PBL pH meter (Figure 7); (c) Effective alkalinitythe capacity of the water to react with hydrogen ions to a pH of 4.5, reported as calcium carbonate,  $CaCO_3$ , in milligrams per liter (mg/l) (Figure 8); (d) Specific conductance - the ion concentrations of the unfiltered sample, reported as micromhos per centimeter at 25 degrees centigrade (µmhos/cm @ 25°C). The specific conductance was obtained through a Beckman Solubility bridge model RB 3338 (Figure 9).

# LABORATORY ANALYSIS

Water samples from the field were returned to the geochemical laboratory and analyzed as soon as possible. This minimized sample deterioration with the passage of time. The water samples were analyzed on a Perkin-Elmer, Model 303 atomic absorption spectrophotometer with a graph recorder readout.

Three laboratory techniques were used in sample analysis:

(1) Flameless method: Mercury analysis, to 0.1 parts per billion (ppb) sensitivity, followed the procedures of the Environmental Protection Agency (1971). These analyses were run first to reduce escape of the volatile mercury vapors after the sample bottle was opened. To destroy any organo-mercury compounds present in the sample, potassium permanaganate and potassium persulfate solutions were added to insure complete oxidation to the mercuric ion prior to analysis. Stannous sulfate was added immediately before attaching the bottle to the aeration equipment. Atomic absorption occured in a special plexiglas tube approximately 1 inch in diameter and 4 1/2 inches in length. This tube was fitted with quartz windows at each end. The tube was



Figure 8: Field determination - effective alkalinity of unfiltered sample.



Figure 9: Field measurement - specific conductance of unfiltered sample.

placed in the position normally occupied by the burner and connected to the sample bottle by rubber tubing. Mercury vapors were carried into the plexiglas tube by the compressed air bubbled through the sample after the stannous sulfate had been added to the sample.

(2) Direct aspiration: Water samples containing zinc and iron, down to 10 ppb, were aspirated directly into the atomic absorption unit with no additional preparation.

(3) Chelation and extraction: Water samples containing copper, lead, cadmium, and sometimes iron (to 1 ppb sensitivity) were analyzed through a chelation/extraction process which enabled accurate measurement by the atomic absorption unit. The metals in the sample were first chelated with ammonium pyrrolidine dithiocarbonate (APDC) and extracted with methyl isobutyl ketone (MIBK). The extract was aspirated into the flame of the spectrometer for measurement of metal content.

#### CALCULATION OF METAL VALUES

In each of the above procedures, standard solutions - and blanks of double-distilled water - of known metal content were analyzed along with the other samples. From a graphic plot of recorder peak height versus known concentration, a standard curve was obtained for the particular element in that group of samples. The comparison of peak height of each sample with the standard curve gave the element concentration in the sample. This concentration is determined in parts per billion (ppb).
#### RESULTS OF HEAVY METALS ANALYSIS

The analytical program was undertaken to determine if any significant amounts of heavy metals are present in the main streams of the James River basin. This primary objective has been met and the results are tabulated in Appendix I, Sample Analyses Data.

Results of the numerous analyses are summarized in Tables 1 and 2. These give the mean, standard deviations, and the extreme values for each element or property investigated for each collection season. A summary of the high metal value at each sample site, regardless of the season of occurrence, is also given.

### SEASONAL VARIATION

Possible seasonal variations were investigated through water sample collections during three distinct seasons of the year. These included: winter of 1972-73 (intermittently wet), spring of 1973 (extremely wet), and summer of 1972 (extremely dry).

Changes in the ratios of means for the individual metals are considered good indicators of seasonal variation. Mean ratios for the various metals and physical properties are listed for winter, spring, and summer, respectively. Copper, 1:0.7:0.7; lead, 1:1:0.5; pH, 1:1:1; and specific conductance, 1:1.1:1.1, show the least seasonal change in means. Greatest seasonal variations in means are shown by mercury, 0.0:0.0:1; cadmium, 1:2.6:1.2; iron, 1:0.5:0.2, zinc, 1:1:1.9; effective alkalinity, 1:1.3:1.8; and temperature, 1:2.4:3.6.

Dilution as a result of increased runoff from winter and spring rains had been expected, but this was not the case. With the exception

	Mercury				Zinc			Copper			Lead			Cadmium			Iron							
Season	MEAN	STD. DEV.	MAX IMUM	MINIMUM	MEAN	STD. DEV.	MAX IMUM	MINIMUM	MEAN	STD. DEV.	MAXIMUM	MINIM	MEAN	STD. DEV.	MAXIMUM	MUMINIM	MEAN	STD. DEV.	MAXIMUM	MUMINIM	MEAN	STD. DEV.	MAXIMUM	MINIMUM
Winton	-	-			15	10			2.9	2.2			2.2	6.6			1.1	1.2			5 <b>9</b>	66		
winter			<0.1	-			46	<10			9.0	<1.0			41	<1.0			7.0	<1.0			277	<1.0
Spring	-	-	<0.1		15	14	64		1.9	3.6	18		2.2	4.2	20		2.9	1.9	7.0		30	26	102	
				-				<10				<1.0				<1.0				<1.0				<10
Summer	0.10	) 0.08	2 0.3	<0.1	29	15	80	<10	2.0	2.2	10	<2.0	1.1	0.47	4.0	<2.0	1.3	1.2	3.0	<2.0	9.7	8.6	40	<2.0
Highest Values from each site re- gardless of season	0.1	0.08	2 0.3	<0.1	31	16	80	<10	4.1	3.6	18	<1.0	3.5	6.9	41	<1.0	3.0	1.9	7.0	<1.0	60	63	277	<1.0

Table 1: Mean, standard deviation, and extremes (ppb) for Hg, Zn, Cu, Pb, Cd, Fe for three sampling periods.

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	Water Temperature				рН				Effective Alkalinity				Specific Conductance			
Season	MEAN	STD. DEV.	MAXIMUM	MINIMUM	MEAN	STD. DEV.	MAXIMUM	MINIMUM	MEAN	STD. DEV.	MAXIMUM	MINIMUM	MEAN	STD. DEV.	MAXIMUM	MUMINIM
	6.2				7.5				84				305			
Winter		2.1				0.45				30				117		
			9.0				8.1				161				750	
				2.0				6.2				30				90
	15				7.6				107				320			
		2.0				0.56				38				91		
Spring	~		22.5				8.9				238				700	
				11				5.9				56				195
••••	22				7.7				153				333			
Summer		2.2				0.33				23				102		
			26				8.3				218				725	
				18				6.7				107				240

Table 2: Mean, standard deviations, and extremes of water temperature (°C), pH, effective alkalinity (CaCO3 in mg/l), and specific conductance ( $\mu$  mhos/cm @ 25°C) of unfiltered samples.

of zinc and mercury, most metal values were higher in the winter and spring seasons. This increase in metal values may be related to a flushing action of the shallow aquifers by the higher groundwater conditions in the winter and spring seasons. Another possibility is an increase in the number of particles <0.45 micron (filter pore size) due to scouring of banks and streambed under high water conditions.

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## VARIABILITY WITHIN STREAM CROSS SECTION

Because of high waters and/or swift currents, it was dangerous or impractical to collect some water samples from visually turbulent zones in the streams. In order to determine if there was significant variance when sampling one part of a stream rather than another, or swift versus calm waters, cross sectional sample profiles of four streams were taken.

These profiles consisted in collection of a sample from the swift turbulent water at mid-stream and one or more samples from the slower waters nearer the banks. Analytical results of one such profile is shown in Table 3. The data indicate that considerable mixing occurred within a very short distance below the confluence of two medium-sized streams under high-water conditions.

Data in Tables 3 and 4 suggest slight differences in dissolved metal content and physical properties from swift to calm waters of a stream, and also suggest differences within the swifter waters. Slight variation is not significant for a reconnaissance survey such as this.

PROFILE SHOWING MIXING



Table 3. Stream cross-sectional profile of heavy metal contents and physical properties showing mixing below confluence, Finley Creek, James River basin, Missouri.

	JA (26	MES RIVER N-22W-8-d	c)		CRANE (26N-24)	CREEK I-29-cd)		J (29	ORDAN CREI N-22W-27-0	EK 1b)
Sample No.	30(W)	30(E)	Avg.	22(W)	22	22(E)	Avg.	51(W)	51(E)	Avg.
Water Temp.	18.0	18.0	18.0	15.5	15.5	15.5	15.5	18.0	18.0	18.0
рН	8.4	7.7	8.1	7.9	8.2	7.8	8.0	7.1	7.3	7.2
Spec. Cond.	345	385	365	320	305	320	315	365	370	368
Нд	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Zn	<10	20	13	20	28	20	23	64	64	64
Cu	1	2	1.5	<1	<]	<]	<1	18	18	18
Pb	<1	<1	< 1	<1	<]	<]	<1	17	19	18
Cd	1	<1	0.8	2	1	2	2	<1	1	0.8
Fe	<50	50	38	<50	<50	<50	<50	90	90	90
Water Speed	Swift	Swift		Slow	Swift	Slow		Swift	Slow	
Stream Depth (ft)	2.5-3	2.5-3		1-1.5	3-4	1-1.5		1.5-2	1-1.5	1-2
Stream Width (ft)			60-70				6-8			4-6

## STREAM CROSS SECTIONAL PROFILES

Table 4: Stream cross sectional profiles of heavy metal contents and physical properties of water samples from James River, Jordan Creek, and Crane Creek, James River basin, Missouri.

## GEO-HYDROLOGIC VARIATION

Valid interpretations of the contribution of any particular stratigraphic unit on heavy metal values and physical properties are very difficult. Water movement has been shown to be directly related to some structures in the area (Harvey and Skelton, 1968). This study referred only to the Springfield area and may not be applicable to the entire basin area.

The habit of two main streams, Finley Creek and James River, further complicates the problem. These streams head in Mississippian strata, flow over Ordovician strata for 20-25 miles, flow again over Mississippian rocks for several miles, then again return to and stay in Ordovician strata. The bedrock throughout the area is predominantly Mississippian rocks. This means that the ground water has percolated through or flowed over an unknown amount of Mississippian and Ordovician rocks prior to reaching a sampled stream. The number of samples from each stratigraphic unit in any one small drainage basin is also too small to yield data of a high confidence level.

Longitudinal schematic geologic profiles of selected streams have been prepared (Figures 10, 11, 12, 13, and 14). These also include graphs of high metal value and specific conductance from each sample site.

Mercury in James River, Finley Creek, and Flat Creek basins is generally higher in areas underlain by Mississippian rocks and may be related to known faulted areas. However, in Wilson Creek basin, an area underlain by Mississippian rocks and having known mineralized



Figure 10: Longitudinal profile using high mercury, lead, copper and cadmium values from water samples from James River, James River basin, Missouri. [F-fault, M-Mississippian, O-Ordovician, N-North, <-flow direction, X-projected mines and prospects].



Figure 11: Longitudinal profile using high iron, zinc and specific conductance values for water samples from James River, James River basin, Missouri. [F-fault, M-Mississippian, O-Ordovician, N-North, <-flow direction, X-projected mines and prospects].



Figure 12: Longitudinal profile using high mercury, lead, copper, cadmium, iron, zinc, and specific conductance values for water samples from Finley Creek, James River basin, Missouri. [Ffault, M-Mississippian, O-Ordovician, E-east, <-flow direction, X-projected mines and prospects].



Figure 13: Longitudinal profile using high mercury, lead, copper, cadmium, iron, zinc, and specific conductance values for water samples from Flat Creek, James River basin, Missouri. [Ffault, M-Mississippian, O-Ordovician, E-east, >-flow direction].



Figure 14: Longitudinal profile using high mercury, lead, copper, cadmium, iron, zinc, and specific conductance values for water samples from Wilson Creek, James River basin, Missouri. [F-fault, M-Mississippian, N-North, <-flow direction, Xprojected mine or prospect].

faults, no mercury was recorded above the lower detection limit, 0.1 ppb.

Zinc content in Flat and Finley Creek waters appears higher in areas of Mississippian rocks where faulting is evident. In the James River zinc content is higher but erratic in places where the stream flows over Ordovician strata. In Wilson Creek zinc values are generally higher than those recorded in other parts of the James River Basin. Higher zinc values occur at the Southwest Springfield Municipal Sewage Treatment Plant (T. 28, R. 22, sec. 7) and at and below an industrial area in the western part of the city.

Copper values are quite low and variable. Higher values occur in Wilson Creek area with a distribution very similar to the high zinc values.

Lead values are generally below detection with two notable areas of exception. These are the upper Wilson Creek industrialized area above the municipal sewage plant, and the extreme upper Flat Creek area.

Cadmium values are erratic with no apparent stratigraphic relations. In Wilson Creek only one cadmium value was above the detection limit. This was below the sewage treatment plant as shown in Figure 7. A known mineralized area is also nearby.

Iron values are generally low. Higher values occur in the eastern portion of the basin in the upper Finley Creek and the upper James River areas. Consistently higher values were recorded in Wilson Creek with the highest values being in the industrialized area and also in the Wilson Creek National Park. Specific conductance appears higher in areas underlain by Mississippian strata. The highest values were recorded at the Springfield sewage plant and in Springfield below the industrial area on Wilson Creek.

# HEAVY METALS CONTENT OF THE STREAM WATERS

#### MERCURY

Very little mercury is present in the streams of the James River basin. Mercury values ranged from below 0.1 ppb to 0.3 ppb. Values above 0.1 ppb occured only in the warm waters of the summer season. This small but notable difference may be related to two factors: (1) warm waters permit more organic growth which could concentrate the mercury (F.W.P.C.A, 1968) and release it upon decomposition of the organic materials, (2) low water conditions reduced the water turbulence and slowed the release of mercury-bearing gases present in the water. Figure 15 illustrates the high mercury values from each sample site.

Detectable mercury exists in many samples; however, these amounts are below the 0.1 ppb reliable detection limit of the atomic absorption unit.

#### ZINC

Zinc contents in the surface streams of the basin range from <10 to 80 ppb. Means for winter and spring (high water conditions) were equal (1:1). Summer means are almost double (1:1.9). The high zinc values from each sample site and the season in which this value was present are illustrated in Figure 16. Concentrations of higher zinc



Figure 15: High mercury values and season of occurrence for water samples from the James River basin, Missouri.



Figure 16: High zinc values and season of occurrence for water samples from the James River Basin, Missouri.

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values in the Springfield-Wilson Creek area are very evident.

Copper content is consistently rather low and uniform from season to season. The ratio of means for the seasons are 1:0.7:0.7. Range in copper values is from <1 ppb to 18 ppb. The most significant concentration of higher copper values is in the Springfield-Wilson Creek area (Figure 17).

#### LEAD

Lead content in the streams of the basin was more variable than expected when compared to the other heavy metals. Considering the extremely low solubility of lead, it was expected that lead values would be much lower than the values for copper and zinc; however, lead values often approached and in some cases exceeded those of copper and zinc. Lead content ranged from lows of <1 ppb to a high of 41 ppb. Most of the higher values were recorded in the winter and spring. Clustering of high values occurs in the Springfield area. Another grouping also occurs in the Cassville-Flat Creek area in the southwestern section of the basin (Figure 18).

## CADMIUM

Cadmium values were consistently low. Range of content was from <1 ppb to 7 ppb. Ratios of means for cadmium (1:2.6:1.2) show the greatest seasonal variation of the metals investigated. Highest cadmium values were present in the spring season (Figure 19). Cadmium content appears to be generally higher in the lower half of the James River basin.



Figure 17: High copper values and season of occurrence for water samples from the James River basin, Missouri.



Figure 18: High lead values and season of occurrence for water samples from the James River basin, Missouri.



Figure 19: High cadmium values and season of occurrence for water samples from the James River basin, Missouri.

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## IRON

Iron content in the basin streams is quite variable from season to season as shown by the ratio of means of 1:0.5:0.2. Variability of values is also quite prevalent within the same season. Iron content for example, ranges from <1 ppb to 277 ppb for the winter season. A concentration of high iron values occurs in the Springfield-Wilson Creek area (Figure 20). Another area of higher iron values occurs on the upper James River at the western boundary of Webster County.

## SPECIFIC CONDUCTANCE

Specific conductance, a measure of the ionic mineral content in the waters, is included in this discussion. The high specific conductance reading at each sample site is illustrated in Figure 21. These range from 165 to 750 micromhos/cm @ 25°C. Means of each seasonal sample set were remarkably uniform with ratios of 1:1.1:1.1.

Highest specific conductance values occur in four areas: (1) Springfield-Wilson Creek and down the James River from Wilson Creek, (2) Flat Creek basin, (3) upper Finley Creek, and (4) Pearson Creek east of Springfield.

# POSSIBLE SOURCES AND SIGNIFICANCE OF HEAVY METALS IN WATER

Properties of water and the heavy metals that were measured in this study are summarized in Table 5. Possible sources for the metals and properties, significance of them, and Public Health Service (PHS) drinking water standards are listed for each.

The purpose of the study was not to classify the James River basin waters according to Public Health Service standards. Yet these do



Figure 20: High iron values and season of occurrence for water samples from the James River basin, Missouri.



Values in micromhos/cm @ 25°C

Figure 21: High specific conductance values and season of occurrence for water samples from the James River basin, Missouri.

provide a basis for comparison of stream waters with others considered acceptable for public drinking water. It should be kept in mind that values given in this report represent dissolved heavy metals (filtered samples). The PHS standards are based on total elemental concentration (unfiltered sample). In areas where unfiltered surface waters do not readily meet PHS standards, filtration is recommended (Public Health Service, 1969).

Property or Metal	Possible Source(s)	Significance
Temperature	Climatic conditions, use of water as a cooling agent, industrial pollution.	Affects usefulness of water for many purposes. Most users desire water of uniformly low temperature. Seasonal fluctuations in temperature of surface waters are comparatively large depending on the volume of water.
Hydrogen-ion concentra- tion (pH)	Acids, acid-generating salts, and free carbon dioxide lower the pH. Carbonates, bicar- bonates, hydroxides, phos- phates, silicates, and borates raise the pH.	A pH of 7.0 indicates neutrality of a solution. Values higher than 7.0 denote increasing alkalinity; values lower than 7.0 denote increasing acidity. pH is a measure of the activity of hydrogen ions. Corro- siveness of water generally increases with decreas- ing pH. However, excessively alkaline water may also attack metals. Recommended PHS limits 6.5-8.5.
Specific conductance (micromhos at 25°C).	Mineral content of the water	Indicates degree of mineralization. Specific conduct- ance is a measure of the capacity of water to con- duct an electric current. It varies with the con- centrations and degree of ionization of the constit- uents, and with temperature.

Table 5: Some properties of water and heavy metals in water with possible sources and significance (modified from Feder, <u>et al</u>., 1969, with additional data from other sources).

Property or Metal	Possible Source(s)	Significance					
Effective Alkalinity (Hardness as (CaCO <sub>3</sub> )	In most waters, nearly all the hardness is due to calcium and magnesium. All the metallic cations other than the alkali metals also cause hardness.	Consumes soap before a lather will form. Deposits soap curd on bathtubs. Hard water forms scale in boilers, water heaters, and pipes. Hardness equivalent to the bicarbonate and carbonate is called carbonate hardness. Any hardness in excess of this is called non-carbonate hardness. Waters of hardness up to 60 mg/l are considered soft; 61-120 mg/l moderately hard; 121-180 mg/l hard; more than 180 mg/l very hard. Recommended limits: 30-500 mg/l.					
Mercury (Hg)	Oxidation of mercury bearing rocks and through disposal of mining, metallurgical, or other industrial waste.	A highly toxic element and undesirable impurity in water. The extreme volatility of this element tends to inhibit toxic accumulations from forming; however, it may become fixed by organic growth and reach toxic levels. The PHS limit (1962) for public drinking water is 5 ppb.					
Zinc (Zn)	Solution of the mineral sphalerite (ZnS), galvanized pipes, and from industrial wastes.	Unusually high concentrations reflect mineralization or man-made pollution. The recommended PHS limit (1962) is 5000 ppb.					

Table 5: (continued)

Property or Metal	Possible Source(s)	Significance
Copper (Cu)	Solution of the mineral chalcopyrite (CuFeS <sub>2</sub> ), copper pipes, and from industrial wastes.	An essential element in nutrition of plants and animals. Excessive amounts may be harmful. PHS (1962) recommends limit of 1000 ppb.
Lead (Pb)	Slightly dissolved from rocks contain- ing galena (PbS). May also be derived from engine exhausts (gaso- line additive) or industrial wastes.	May be highly toxic. Low solubility at common pH levels (6.5-8.5), generally inhibits toxic accumulations. PHS (1962) has mandatory limit of 50 ppb for public drinking water.
Cadmium	Weathering of the mineral greenockite (CdS) or industrial wastes.	Considered toxic in sufficient concentrations. Natural concentrations are generally very low - higher amounts may indicate man-made pollu- tion or mineralization. Mandatory PHS (1962) limits for public drinking water are 10 ppb.
Iron (Fe)	Solution of pyrite and marcasite from rocks and weathering of iron-bearing clays. Also from iron pipes, field or lab equipment, trash dumps, rust- ing automobiles, and industrial wastes. Iron > 1 or 2 ppm in surface water generally indicates acid wastes from mine drainage or other sources.	Quantities greater than 300 ppb cause unpleasant taste, favor growth of iron bacteria, and may cause discoloration in textile manufac- turing, laundry uses, beverage preparation, etc. The PHS recommended limit is 300 ppb for public drinking supplies.

Table 5: (continued)

#### SUMMARY AND CONCLUSIONS

An almost 25 percent population growth from 1960-70 has increased demand on the water resources of the James River basin. Many old lead-zinc mines and prospects in the James River basin and the industrial plants in the Springfield area are potential sources for the addition of dissolved heavy metals to the streams of the basin. The study was begun to determine if significant amounts of the heavy metals - mercury, zinc, copper, lead, cadmium, and iron exist in the waters of the James River basin.

Main streams of the James River basin contained varying quantities of all metals sought in the research program. As a generalization, concentrations of all the heavy metals are in the low parts per billion range.

Mercury in the waters was observed only in the summer season, and in all cases in quantities of 0.3 ppb or less. The geographic distribution appears to relate to known mineralized areas on Flat Creek, Finley Creek, and the upper James River. There are exceptions. Perhaps unknown mine prospects, mineralized areas, or man-made pollution sources exist in these exceptional areas. Relatively higher concentrations were not noted in the Springfield-Wilson Creek area.

Zinc contents in the stream waters range from <1 ppb to 80 ppb. Zinc values are quite variable. Higher values occur in the Springfield area. Another higher level of zinc occurs in waters of the upper James River and its tributaries in Webster County.

Copper values are consistently quite low. These range from <1 ppb

to 18 ppb. Higher values occur in the urban Springfield area and down Wilson Creek. Other high copper values occur on Crane Creek and James River in northern Stone County. One tributary of Flat Creek in northern Barry County drains a mineralized area and has higher copper values.

Lead values range from <1 to 41 ppb and are more variable than expected. Lead values approach and sometimes exceed values for copper and zinc. Higher lead values occur in the Springfield area on a tributary to Wilson Creek in northwestern Christian County, and on Flat Creek and several of its tributaries.

Cadmium ranges from <1 ppb to 7 ppb. The higher values occur primarily in the spring season. Higher values occur on Flat Creek and its tributaries and on Crane Creek and James River in northern Stone County.

Iron content in the streams is highly variable. Content ranges from <1 to 277 ppb. Concentrations of higher values occur in the Springfield and Wilson Creek areas. Higher values also were recorded on the James River and its tributary at the western boundary of Webster County and in the upper end of Lake Springfield in southern Green County.

Specific conductance values range from 90 to 750 micromhos/cm @ 25°C. The higher values are in the Springfield-Wilson Creek area and the James River in northern Stone County. The means from each seasonal sample set do not vary greatly.

Values of zinc, copper, lead, and iron are higher in the Springfield area than below the municipal sewage treatment plant on Wilson Creek. This suggests that the sewage treatment plant is not a source

for dissolved heavy metals. It also suggests that the industrialized area of western Springfield is a source for dissolved heavy metals.

Seasonal variation is apparent with mercury, cadmium, iron, and zinc showing the greatest variance. Expected dilution by runoff of winter and spring rainfall was not indicated. The metals, except zinc and mercury, have generally higher values in the winter and spring seasons.

Variability within different parts of the stream cross-section at the sample site was investigated. This variability does not appear to be of great importance in these turbulent streams.

Variations directly attributable to geo-hydrologic contributions are very difficult to recognize. The variable lithology and age, and lack of detailed geologic mapping complicates this problem. Higher metal values grossly relate to mineralized and faulted areas in Flat Creek, Finley Creek, Wilson Creek, and upper James River areas. Streams crossing areas underlain by Mississippian rocks also have some higher metal values. However, the small number of samples does not give a high level of confidence to these conclusions. The Springfield area is especially complicated as it not only is an urban industrial area, but also has known mineralization in the Mississippian strata within the immediate area.

All heavy metal values in the waters were below Public Health Service standards for drinking water. This study, however, involved only dissolved metals in a filtered sample.

Dissolved metals in the main streams of the James River basin should not constitute a pollution problem for plant or animal life. If some of the waters where higher heavy metal contents were observed were to be used without filtration, supplemental studies on the heavy metal contents of unfiltered samples should be conducted.

As a possible research application, more detailed sampling and analysis of stream waters and sediments for heavy metals might yield results which would permit identification of mineralized areas and unrecognized fault zones.

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### VITA

Richard Jerome Lance was born on June 20, 1946, in Blairsville, Georgia. He attended primary and secondary schools in Blairsville, Georgia and Detroit, Michigan. He received the Bachelor of Science in Geology at the University of Georgia in Athens, Georgia, in June 1968. He subsequently entered the military service.

In June 1969, upon completion of Officer Candidate School at Yorktown, Virginia, he received a commission as Ensign in the United States Coast Guard. He served at Charleston, South Carolina in the capacities of Operations Officer, Port Safety Officer, and Personnel Officer until June 1972.

Richard married the former Margaret Rachel Schultze of Columbia, South Carolina, in September 1969. They have one daughter, Rebecca Dianne.

Richard enrolled in the Graduate School of the University of Missouri-Rolla in July 1972. He held the V. H. McNuttGraduate Fellowship from September 1972 through December 1973.

## APPENDIX I

## SAMPLE ANALYSES DATA

The appended data were obtained during collection and analysis of water samples from main streams in the James River basin of southwestern Missouri.

Column headings are mainly self-explanatory. Number designations of sample locations are the same as those shown in Figure 3. The General Land Office Survey System is used for township, range, section, quarter section, and quarter-quarter section. Seasons are designated by W-winter 1972-73, S - spring 1973, and SU - summer 1972. Effective alkalinity is reported as  $CaCO_3$  in mg/l. Specific conductance is given in  $\mu$  mhos/cm @ 25°C.
Sample	Sea-	Water		Effective	fective Specific	Meta	al Valu	es (pa	rts pe	r bill	ion)
Location	son	Temp(°C)	рН	Alkalinity	Conductance	Hg	Zn	Cu	Pb	Cd	Fe
1	W	7.5	7.7	67	280	<0.1	21	4	<1	<]	190
29N-19W-17-bb	S	13.5	7.6	77	260	<0.1	10	<]	2	5	35
	SU	22.0	7.6	167	305	0.2	55	<2	<2	<2	5
2	W	7.0	7.6	54	225	<0.1	21	4	<]	2	240
29N-19W-8-ac	S	14.0	7.5	66	245	<0.1	<10	<]	1	3	25
	SU	22.0	7.4	107	240	<0.1	55	<2	<2	3	22
3 29N-18W-6-ac	W	7.0	6.5	59	240	<0.1	31	2	<]	<]	32
	S	14.5	7.6	59	225	<0.1	<10	<]	<]	1	35
	SU	22.0	7.6	110	240	0.2	35	<2	<2	<2	5
٨	W	7.0	7.7	64	220	<0.1	18	1	<1	2	50
4 20N-19W-5-25	S	14.5	7.7	62	220	<0.1	10	<1	<]	3	<10
29N-10W-5-ab	Su	22.0	7.4	135	245	<0.1	16	<2	<2	3	40
F	W	7.0	6.2	62	235	<0.1	13	2	<]	<]	60
20N_18W_12_ad	S	14.5	7.7	59	240	<0.1	14	1	<]	3	35
29N-10W-12-44	SU	21.8	7.2	135	250	<0.1	55	<2	<2	<2	17
c	W	7.5	7.0	74	240	<0.1	18	2	<]	2	31
20N 10U 22 ca	S	14.5	7.1	71	230	<0.1	<10	1	<1	1	22
2011-10W-23-Ca	SU	24.0	7.6	161	300	<0.1	16	<2	<2	<2	11
7	W	8.5	7.8	77	280	<0.1	21	1	<]	<]	33
/ 2011 194-22-64	S	14.5	7.3	77	265	<0.1	<10	<]	<1	2	25
2011-10W-23-DU	SU	21.0	7.3	167	270	<0.1	35	<2	<2	<2	11

Sample	Sea-	Water		Effective	Specific	Meta	l Value	s (pai	rts pe	r billi	on)
Location	son	Temp(°C)	рН	Alkalinity	Conductance	Hg	Zn	Cu	P.b	Cd	Fe
8 28N-18W-24-cb	W S SU	6.5 14.5 22.0	6.8 7.8 7.2	69 66 144	245 230 295	<0.1 <0.1 0.2	13 <10 35	1 1 <2	<1 <1 <2	2 3 <2	30 <10 <2
9 27N-19W-12-ba	W S SU	7.0 13.5 21.0	6.9 7.9 6.7	57 90 138	170 265 280	<0.1 <0.1 0.2	13 10 35	2 <1 <2	<1 <1 <2	<1 2 <2	17 <50 5
10 27N-19W-1-ca	W S SU	6.0 14.5	7.1 7.0 7.7	77 131 151	280 365 300	<0.1 <0.1 <0.1	27. 10 35	3 <1 <2	<1 <1 <2	<1 1 3	20 <50 11
11 27N-19W-18-db	W S SU	7.5 15.0 21.0	7.8 7.8 7.6	75 123 138	265 220 280	<0.1 <0.1 <0.1	13 25 16	2 1 <2	<1 <1 <2	2 1 < 2	33 <50 5
12 27N-20W-18-cb	W S SU	7.5 16.0 24.0	7.8 8.1 7.7	77 116 138	275 235 280	<0.1 <0.1 0.2	13 10 55	2 <1 <2	<1 <1 <2	7 2 <2	30 <50 11
13 26N-22W-1-bd	W S SU	7.5 16.0 25.0	7.4 7.8 8.0	82 133 162	295 315 280	<0.1 <0.1 0.2	<10 10 16	1 <1 <2	<1 <1 <2	<1 2 <2	20 <50 5
14 23N-27W-3-cd	W S SU	2.5 16.0 19.5	6.5 7.6	67 146	230 390 270	<0.1 <0.1 0.3	46 <10 16	5 1 <2	41 16 <2	3 7 <2	16 <10 15

Sample	Sea-	Water		Effective	Specific	Metal Values (parts per billion)						
Location	son	Temp(°C)	рН	Alkalinity	Conductance	Hg	Zn	Cu	Pb	Cd	Fe	
15	W	4.5			270	<0.1	24	5	4	<2	43	
24N-27W-12-ca	S SU	14.5 21.0	8.3 7.7	72 135	290 255	<0.1 0.2	10 35	<1 <2	<1 <2	7 <2	<10 5	
16 24N 27U 1 55	W	4.0	75	60	275	<0.1	24 23	7 <1	23 <1	4	34 <10	
24N-27W-1-ab	SU	18.0	7.5	141	280	0.2	16	<2	<2	<2	<2	
17 24N-26W-24-aa	W S SU	2.5 16.0 22.0	7.7 7.6	90 194	340 315 340	<0.1 <0.1 <0.1	10 <10 16	3 <1 <2	<2 <1 <2	<2 3 <2	38 13 5	
18 24N-26W-24-ad	W S SU	3.5 14.0 22.0	7.9 8.0	56 128	295 260 285	<0.1 <0.1 0.3	10 10 16	5 <1 <2	<2 4 <2	<2 5 <2	37 <10 5	
19 23N-25W-6-ca	W S SU	2.0 15.0 20.0	8.0 7.5	90 167	260 300 330	<0.1 <0.1 0.1	<10 <10 <10	<2 4 <2	10 2 <2	2 3 <2	21 <10 5	
20 24N-24W-30-da	W S SU	2.5 15.5 24.5	8.2 8.1	87 136	255 235 255	<0.1 <0.1 <0.1	<10 <10 16	3 <1 <2	<2 4 <2	<2 5 <2	25 13 11	
21 24N-24W-17-dc	W S SU	2.5 13.0 18.5	7.9 7.3	95 197	260 315 375	<0.1 <0.1 0.3	10 <10 35	2 <1 <2	<2 2 <2	2 7 <2	33 <10 <2	

Sample	Sea-	Water		Effective Specific	Meta	Metal Values (parts per billion)						
Location	son	Temp(°C)	рН	Alkalinity	Conductance	Hg	Zn	Cu	Pb	Cd	Fe	
22 26N-24W-29-cd	W S SU	6.5 15.5 21.0	7.3 8.0 7.8	82 135 167	240 315 315	<0.1 <0.1 0.1	<10 23 35	<1 <1 <2	<1 <1 <2	<1 2 <2	19 <50 <2	
23	W	4.0			340	<0.1	10	5	<2	<2	32	
23N-23W-17-db	SU	19.0	8.2	161		<0.1	20	<2	<2		8	
24 24N-23W-7-cb	W S SU	3.5 14.0 21.0	7.2 8.2	84 156	375 300	<0.1 <0.1 <0.1	13 <10 38	9 <1 <2	<2 <1 <2	<2 <1	35 50 8	
25 25N-24₩-1÷cd	W S SU	6.5 15.0 19.0	7.3 8.0 7.7	75 123 167	240 300 305	<0.1 <0.1 <0.1	<10 25 38	<1 <1 10	<1 <1 <2	<1 3	20 <50 6	
26 25N-23W-6-ab	W S SU	6.0 16.0 23.0	7.8 8.2 8.2	89 130 148	335 330 300	<0.1 <0.1 <0.1	<10 10 38	1 1 <2	<1 2 <2	<1 7	10 <50 7	
27 25N-23W-9-dc	W S SU	5.0 16.5 26.0	7.8 8.2 7.6	79 123 143	310 300 310	<0.1 <0.1 <0.1	<10 10 38	<1 <1 <2	<1 <1 <2	<1 4	20 <50 15	
28 25N-23W-1-aa	W S SU	7.5 17.5 24.5	7.7 8.9 8.1	87 151 161	325 310 465	<0.1 <0.1 <0.1	<10 20 38	1 1 8	<1 <1 <2	<1 4	35 <50 8	

Sample	Sea-	Water		Effective	Specific	Metal Values (parts per billion)						
Location	son	Temp(°C)	рН	Alkalinity	Conductance	Hg	Zn	Cu	Pb	Cd	Fe	
29	W	7.5	7.5	77	280 280	<0.1 <0.1	<10 <10	] <1	<] 3	<1 6	20 <50	
25N-23W-12-da	SU	22.0	8.1	144	285	0.1	20	<2	<2	Ū	3	
30 26N-22W-8-dc	W S SU	9.0 18.0 25.0	7.6 8.1 7.7	95 156 176	350 365 575	<0.1 <0.1 <0.1	12 13 20	1 2 <2	<1 <1 <2	<] ]	20 <50 24	
31 26N-22W-8-dd	W S SU	7.0 16.5 26.0	7.5 8.6 8.1	82 146 154	390 285 350	<0.1 <0.1 <0.1	<10 10 20	<1 <1 <2	<1 <1 <2	<1 2	32 <50 < 2	
32 27N-22W-32-ab	W S SU	8.5 18.5 24.0	7.3 8.2 7.9	92 156 148	280 385 420	<0.1 <0.1 <0.1	12 20 20	3 1 2	<1 <1 <2	<] ]	60 <50 15	
33 27N-22W-5-bc	W S SU	19.0 23.0	7.3 8.1	141 146	400 380	<0.1 <0.1	20 20	1 5	2 <2	3	<50 3	
34 28N-23W-35-cd	W S SU	7.5 14.5 18.0	7.8 7.5 7.8	105 166 187	405 430 370	<0.1 <0.1 <0.1	<10 13 38	1 <1 <2	<1 <1 4	<] ]	33 <50 8	
35 28N-23W-25-cb	W S SU	8.0 14.5 23.0	7.1 7.5 7.5	136 139 164	440 500 485	<0.1 <0.1 <0.1	30 <10 20	6 3 <2	<1 <1 <2	<] ]	277 70 24	

Sample	Sea-	Water		Effective	Specific	Meta	al Valu	es (pa	rts pe	r bil	lion)
Location	son	Temp(°C)	рН	Alkalinity	Conductance	Hg	Zn	Cu	Pb	Cd	Fe
36	W	8.0	6.7	136	465	<0.1	19	3	<]	<]	94
28N-23W-24-bc	S SU	14.0 24.0	6.7 7.6	174	390 520	<0.1 <0.1	15 20	3 4	<1 <2	1	70 22
37	W	7.5	8.1	62	230	<0.1	19	3	<] <]	<]	140
29N-20W-31-bb	s SU	22.0	7.9	128	275	<0.1 <0.1	20	4	<2	5	5
38	W	9.0	8.1	102	380 375	<0.1	19 15	3 ~1	2	<] 5	20 13
29N-21W-35-ab	SU	19.0	7.8	189	400	<0.1	20	2	<2	J	6
39	W	8.5	7.5	92	265	<0.1	<10	] <]	1	<] 3	100
28N-21W-15-cc	SU	25.5	8.3	126	260	<0.1	20	2	<2	5	2
40	W	7.5	7.2	85 130	300 320	<0.1	12 13	3 4	1	<] 2	46 <50
28N-21W-30-ac	SU	24.0	7.8	135	295	<0.1	20	5	<2	2	6
41	W	6.0	7.1	161 238	750 700	<0.1	37 20	8	1	<] 2	110
29N-22W-7-aa	SU	25.5	7.5	218	725	<0.1	80	8	<2	L	29
42 24N-27W-12-bc	W S SU	4.0 14.0	7.9	75	280 310	<0.1 <0.1	17 11	3 <1	<2 2	<2 5	35 <10

Sample Location	Sea-	Water Temp(°C)	рН	Effective Alkalinity	Specific	Meta	al Valu 7n	es (pa	rts per Pb	r bill Cd	ion) Fe
		· · · · · · · · · · · · · · · · · · ·									
43 24N-23W-7-ca	W S SU	2.5 15.5	7.7	102	320 230	<0.1 <0.1	10 <10	2 <1	<2 2	<2 3	44 <10
44 26N-24W-29-cc	W S SU	5.5	7.5	39	165	<0.1	<10	3	1	<]	56
45 29N-22W-27-cb	W S SU	3.0 18.0	7.7 7.3	156 116	720 375	<0.1 <0.1	12 64	4 11	<1 3	<] ]	92 102
46 29N-22W-29-cb	W S SU	5.0 18.0	7.4 6.7	148 97	480 360	<0.1 <0.1	27 42	3 15	<1 7	<1 1	38 102
47 28N-17W-7-ba	W S SU	8.0 13.5	7.9 7.8	80 74	285 265	<0.1 <0.1	18 <10	1 1	<1 <1	2 4	30 13
48 28N-17W-20-dd	W S SU	7.0 14.0	7.6 7.6	72 67	210 235	<0.1 <0.1	18 14	 <]	2 <1	2 1	20 59
49 29N-22W-26-cc	W S SU	9.0 16.5	8.0 7.2	30 131	90 375	<0.1 <0.1	21 35	7 7	<1 20	2 1	220 <50

Sampl Locat	e cion	Sea- son	Water Temp(°C)	pН	Effective Alkalinity	Specific Conductance	Meta Hg	l Valu Zn	ies (par Cu	rts pe Pb	r bill Cd	ion) Fe
5 29N-2	50 22W-23-bc	W S SU	7.5	7.4	36	165	<0.1	45	8	<]	<]	253
5 29N-2	51 22W-27-db	W S SU	18.0	7.2	113	368	<0.1	64	18	18	1	90
29N-3	52 22W-28-bb	W S SU	17.5	6.8	180	565	<0.1	42	3	<]	1	90
29N-	53 21W-35-ac	W S SU	9.0 11.5	8.3 7.6	105 108	385 380	<0.1 <0.1	<10 11	2 <1	<] <]	<] 3	10 <10