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

Paul Dean Proctor Richard J. Lance

# Missouri Water Resources Research Center University of Missouri

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# Abstract

Demand for water in the James River basin has greatly increased. Larger numbers of industrial plants and the presence of lead-zinc prospects in the basin are potential sources of heavy metal additions to the waters of the area. This study determines selected heavy metal content and distribution in the streams of the basin and establishes some heavy metal bench mark values for this time period.

Approximately 50 water samples were collected in each of three seasons. These samples were analyzed by atomic absorption techniques. Temperature, specific conductance, pH, and effective alkalinity were made in the field.

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 geógraphic variations are also apparent. Heavy metal contributions appear to be related to mineralized and faulted areas in the basin. Variation of heavy metals

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 AND OBJECTIVES

The presence of many old lead-zinc mines and prospects in southwestern Missouri has raised concern that ground and surface waters may be receiving additions of heavy metals from these mineralized areas. The scenic beauty of this area and 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 and become a part of the food chain for the region. Hence, amount and kind of dissolved heavy metals in the waters may determine possible uses and non-uses of stream waters.

The major objective of the study was 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 area is on the fringe of the intensely mineralized Tri-State zinc mining district. Several small mineralized areas are within the basin itself. Springfield, the third most populous city of the state, is on the northern edge of the basin.

Because of this major city, a second objective was to compare natural heavy metal additions with those which possibly were contributed by an industrialized and densely populated area.

While several other objectives were outlined in the original proposal to study heavy metal content of streams, springs, and subsurface waters within the James River basin and their possible source, the very low-key funding of the project permitted only restricted sampling and analyses of stream waters on a reconnaissance basis.

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. Based on funding and time availability, a reconnaissance sampling of the main stream waters of the James River basin of southwest Missouri was outlined to determine heavy metal content and distribution. Three distinct seasons of the year were selected and about 50 water samples collected during each season. Analytical techniques, using a Perkin-Elmer Model 303 atomic absorption spectrophotometer, were initiated for lead, zinc, copper and iron metals common to the nearby Tri-State mining district. The more toxic cadmium and mercury were included in the analyses.

At least two possible sources of heavy metals to the waters were considered: (1) small structurally controlled mineralized areas within the basin and, (2) industrial areas within Springfield. Determination of the actual sources was a major part of the problem. A third part of the problem was to establish time-based bench mark levels for selected heavy metals in the stream waters of the basin. These bench mark values of heavy metals should act as references for later water quality studies as population and industry increase in the area.

The area involved comprises some 1500 square miles and includes portions of Barry, Stone, Lawrence, Christian, Greene, Douglas and Webster Counties in southwestern Missouri.

The study of the heavy metal content of the streams of the James River basin included four major phases: (1) review of the literature, (2) reconnaissance field sampling of the main streams during three distinct seasons, (3) analyses of the water samples and, (4) interpretation of the results.

# Previous Work

Shepard (1898) studied the geology and mineral occurrences of Greene and portions of surrounding counties. Clark and Beveridge (1952) studied the stratigraphy of the area and Vineyard and Fellows (1967) did later work. Feder (1969) reported on water resources of the Joplin area and presented data on zinc and sometimes iron and copper. After several fish kills along the James River, Harvey and Skelton (1968) and the F.W.C.P.A. (1969) studied the possible pollution contributions from the Southwest Springfield Sewage Treatment Plant and industries in the Wilson Creek area of western Springfield. Heavy metals were not included in these studies. Miesch, et al., (1970) reported on very broad reconnaissance sampling of trace metals in the waters, sediments, soils and plants of the state. No samples are reported from the James River basin. Decker, et al., (1973, personal communication) are monitoring heavy metals in the streams of southwest Missouri. The Office of Industrial Waste Surveillance and Enforcement is also currently monitoring effluents from the city's industries (1973, H. Criswell, personal communication).

Proctor, et al, (1973) reported on heavy metals in the waters of the Springfield and Joplin areas. Head (1973) recently completed a reconnaissance study of cadmium, copper, lead and zinc in the fine fractions of sediments in the James River basin.

# Field Sampling and Tests

Approximately fifty preliminary stream sample sites were selected in the office using accessibility, uniformity of coverage and closeness to established stream gaging stations as criteria (Fig. 1). These were adjusted in the field as needed. Three active stream gaging, water quality stations of the United States Geological Survey (1971) were included as sample sites in this study. They supplied data on seasonal changes in stream flow. Because of the population and industry density in the Springfield area, the number of samples was greater than in less populated areas in the basin. Some sites were dry in the latter area because of a summer dry spell, but these were later sampled during the wet winter and spring seasons of 1972-73 (Fig. 1).

Field sampling and analytical methods closely followed those described by Brown, <u>et al.</u>, (1970) with minor modifications. Water samples were taken from the swift turbulent waters to give the best mixed sample (Fig. 2). Collections were always upstream from highway bridge crossings. A oneliter part of the sample was filtered through a 0.45 micron membrane filter and placed in an acid cleaned polyethylene



Figure 1. Location map of main stream sample sites, James River basin, Mişsouri.



Figure 2. Typical sample site - Flat Creek. Sample taken from turbulent water zone.



Figure 3. Field filtration of sample using the Skougstad filter assembly.

bottle (Fig. 3). The filtrate was acidified with 10 ml of reagent grade 1:1 nitric acid and then tightly capped until time of analysis (Fig. 4).

Temperature of the water, pH, effective alkalinity and specific conductance were determined directly in the field. A battery operated Sargent-Welch pH meter (Fig. 5), titration (Fig. 6), and a Beckman Solubility Bridge model RB-3338 (Fig. 7) were used for the latter three tests.

# Laboratory Analysis

Watersamples were analyzed as soon as possible after collection in the laboratory on a Perkin-Elmer Model 303 absorption spectrophotometer with a graph recorder readout.

Flameless, direct aspiration, and chelation and extraction were the three analytical methods used. For mercury analysis the flameless method permitted ready detection to 0.1 parts per billion (ppb) following procedures outlined by the EPA (1971). These were run first to reduce loss of the volatile mercury after the sample bottle was opened.

Zinc and iron down to 10 ppb were aspirated directly into the atomic absorption unit without additional preparation.

Copper, lead, cadmium and sometimes iron (to 1 ppb sensitivity) were analyzed using the chelation/extraction process. Metals in the sample.were chelated with ammonium pyrrolidine dithiocarbonate (APCD) and then extracted with methyl isobutyl ketone (MIBK). The extract was aspirated into the flame of the spectrometer for measurement of metal content.

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Figure 4. Sample acidification for retention of dissolved metals until analysis.







Figure 6. Field determination - effective alkalinity of unfiltered sample.



Figure 7. Field measurement - specific conductance of unfiltered sample.

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In each of the procedures, standard solutions, and blanks of double-distilled water of known metal content were analyzed along with the water sample. A standard curve was obtained from a graphic plot of recorder peak height versus known concentration. By comparing the peak height of each sample with the standard curve, one obtains the element concentration in the sample in parts per billion.

# Geologic Setting of Samples

Because of the known preferred occurrence of zinc-leadcopper and minor cadmium sulfides in the Mississippian rocks of the nearby Joplin mining area, a geologic map compilation from all possible sources was made. This appears as figure 8. The stratigraphy of the area is shown in figure 9 beginning with the Gasconade dolomite. Within the area, streams cut as low as the Jefferson City dolomite as shown.

As a general view, most of the rocks in the James River basin are of marine origin and comprise parts of the Ordovician, Devonian, Mississippian and Pennsylvanian Systems of the Paleozoic Era. Surficial sediments locally cover these older rocks. Only a small part of the area has been geologically mapped in any detail (Clark, 1941; Fellows, 1970; Beveridge, 1970). Reconnaissance geologic mapping suggest some fold structures and several faults (McCracken, 1971). The known folds trend generally westerly to northwesterly. Displacements on the faults approximate 50-60 feet up to 140 feet. In southwestern Barry County a fault has vertical displacement of 250 feet.



Figure 8. Generalized geologic map of James River basin, Missouri showing mineralized areas (compiled by W. J. Head and R. J. Lance, 1973).

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Figure 9. Stratigraphic section of James River basin. Exposures mainly include units above the Roubidoux Formation.

Base Metal Mineralization

Base metal mineralization occurs mainly in the Mississippian strata in the James River basin (Shepard, 1898). Most of it occurs in the present Burlington-Keokuk and Northview formation (Fig. 9). Sphalerite (ZnS), galena (PbS), pyrite (FeS<sub>2</sub>), and possibly minor greenockite (CdS) have been reported together with lesser copper sufides as minor replacement masses and fillings in breccia zones and with solution features.

# Streamflow and 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, 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 the caverns have collapsed and formed sinkholes. In many areas, solution activity is also evident along bedding planes, lithologic changes, joints, and faults. Areas of mineralization may also be affected by the surface and groundwater activity.

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 offluent dispersal 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 8, 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.

#### RESULTS OF HEAVY METALS ANALYSES

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   |  |  |   |   |  
   |  |   |
|-------------------|-----------|-------------|---|--|---|--
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---|--|---|--|---|--|---|--|--|--|---|---
--|--|---|
| MEAN<br>STD. DEV. | MAXIMUM   | MINIMUM     | MEAN  | STD. DEV.  | MAXIMUM   | MININIM  | MEAN   
   
  | STD. DEV.  
   
  | MAXIMUM  | WIWINIW   | MEAN   | STD. DEV.   | MUMIXAM  | MUMINIM   | MEAN   | STD. DEV.  | MAXIMUM  | WINIM   | MEAN  | STD. DEV.  
   | MAXIMUM  | MUMINIM   |
| -<br>             |           |             | 15  | 10 -   |   |  | 2.9  
   
  | 2.2  
   
  |  |   | 2.2  | 6.6   |  |   | 1.1  | 1.2  |  |   | 59  | 66   
   |  |   |
|                   | <0.1      | -           |   |  | 46<br><   | 10   |  
   
  |  
   
  | 9.0  | )<br><1.0   |  |   | 41   | <1.0  |  |  | 7.0  | <1.0  |   |  
   | 277  | <1.0  |
| -                 | <0.1      | -           | 15  | 14   | 64  | 10   | 1.9  
   
  | 3.6  
   
  | 18   | <1.0  | 2.2  | 4.2   | 20   | <1.0  | 2.9  | 1.9  | 7.0  | <1.0  | 30  | 26   
   | 102  | <10   |
| 0.10<br>0.08      | 32<br>0.3 | -<br><0.1   | 29  | 15   | 80<br><1  | 0  | 2.0  
   
  | 2.2  
   
  | 10   | <2.0  | 1.1  | <b>0.4</b> 7  | 4.0  | <2.0  | 1.3<br>1   | 1.2  | 3.0  | <2.0  | 9.7   | 8.6  
   | ,<br>40  | <2.0  |
| 0.10<br>0.08      | 2<br>0.3  | -0.1        | 31  | 16   | 80  | 10   | 4.1  
   
  | 3.6  
   
  | 18   |   | 3.5  | 6.9   | 41.  |   | 3.0  | 1.9  | 7.0  |   | 60  | 63   
   | 277  |   |
|                   | Mero      | Mercury<br> | Mercury<br>Mercury<br>Mercury<br>Mercury<br>Mercury<br>Mercury<br>Mummu<br>Mummu<br>-<br>-<br>-<br>-<br>-<br>-<br>-<br>-<br>-<br>-<br>-<br>-<br>- | Mercury       Mercury         N       N       N         N       O       O         -       -       15         -       -       15         -       -       15         -       -       15         -       -       15         -       -       15         -       -       15         -       -       15         -       -       15         -       -       15         -       -       15         -       -       15         -       -       15         -       -       -         0.10       29       -         0.10       31       -         0.082       0.3       -         0.3       -       - | Mercury       Zin         Nercury $2in$ Nercury $in$ NH       N         NH       N         N $in$ | Mercury       Zinc         Nercury       Zinc         Name       Name         Na | Mercury         Zinc           Nad         MM         NM $Ad$ $Ad$ MM $Ad$ <td>Mercury         Zinc           N         <td< td=""><td>Mercury         Zinc         Cop           <math>\dot{A}</math> <math>\dot{A}</math></td><td>Mercury         Zinc         Copper           N</td><td>Mercury         Zinc         Copper           <math>N = 0</math> <math>- 0</math> <math>15</math> <math>2.9</math> <math>2.2</math> <math>9.0</math> <math>- 0</math> <math>- 0</math></td><td>Mercury         Zinc         Copper           <math>NW</math> <math>NW</math></td><td>Mercury         Zinc         Copper         Lea           <math>NW</math> <math>MW</math> <math>NW</math> <math>MW</math>         &lt;</td><td>Mercury         Zinc         Copper         Lead           <math>NVWW</math> <math>NWWWW</math> <math>NWWWWWW</math> <math>NWWWWWWWWWWWWWWWWWWWWWWWWWWWWWWWWWWWW</math></td><td>Mercury         Zinc         Copper         Lead           <math>NV = M</math> <math>NV = M</math></td></td<><td>Mercury         Zinc         Copper         Lead           <math>NPH</math> <math>NPH</math></td><td>Mercury         Zinc         Copper         Lead         Cadn           <math>NPBW</math> <math>NPSW</math> <math>NPSW</math></td><td>Mercury         Zinc         Copper         Lead         Cadmium           <math>NPBW</math> <math>NPBW</math></td><td>Mercury         Zinc         Copper         Lead         Cadmium           <math>N_{HO}</math> <math>N_{HO}</math></td><td>Mercury         Zinc         Copper         Lead         Cadmium           <math>NPW</math> <td< td=""><td>Mercury         Zinc         Copper         Lead         Cadmium         Irc           <math>Mercury</math> <math>Mercury</math></td><td>Mercury         Zinc         Copper         Lead         Cadmium         Iron           <math>NY = 0</math> <math>NY = 0</math></td></td<></td></td> | Mercury         Zinc           N <td< td=""><td>Mercury         Zinc         Cop           <math>\dot{A}</math> <math>\dot{A}</math></td><td>Mercury         Zinc         Copper           N</td><td>Mercury         Zinc         Copper           <math>N = 0</math> <math>- 0</math> <math>15</math> <math>2.9</math> <math>2.2</math> <math>9.0</math> <math>- 0</math> <math>- 0</math></td><td>Mercury         Zinc         Copper           <math>NW</math> <math>NW</math></td><td>Mercury         Zinc         Copper         Lea           <math>NW</math> <math>MW</math> <math>NW</math> <math>MW</math>         &lt;</td><td>Mercury         Zinc         Copper         Lead           <math>NVWW</math> <math>NWWWW</math> <math>NWWWWWW</math> <math>NWWWWWWWWWWWWWWWWWWWWWWWWWWWWWWWWWWWW</math></td><td>Mercury         Zinc         Copper         Lead           <math>NV = M</math> <math>NV = M</math></td></td<> <td>Mercury         Zinc         Copper         Lead           <math>NPH</math> <math>NPH</math></td> <td>Mercury         Zinc         Copper         Lead         Cadn           <math>NPBW</math> <math>NPSW</math> <math>NPSW</math></td> <td>Mercury         Zinc         Copper         Lead         Cadmium           <math>NPBW</math> <math>NPBW</math></td> <td>Mercury         Zinc         Copper         Lead         Cadmium           <math>N_{HO}</math> <math>N_{HO}</math></td> <td>Mercury         Zinc         Copper         Lead         Cadmium           <math>NPW</math> <td< td=""><td>Mercury         Zinc         Copper         Lead         Cadmium         Irc           <math>Mercury</math> <math>Mercury</math></td><td>Mercury         Zinc         Copper         Lead         Cadmium         Iron           <math>NY = 0</math> <math>NY = 0</math></td></td<></td> | Mercury         Zinc         Cop $\dot{A}$ | Mercury         Zinc         Copper           N | Mercury         Zinc         Copper $N = 0$ $- 0$ $15$ $2.9$ $2.2$ $9.0$ $- 0$ | Mercury         Zinc         Copper $NW$ | Mercury         Zinc         Copper         Lea $NW$ $MW$ $NW$ $MW$ < | Mercury         Zinc         Copper         Lead $NVWW$ $NWWWW$ $NWWWWWW$ $NWWWWWWWWWWWWWWWWWWWWWWWWWWWWWWWWWWWW$ | Mercury         Zinc         Copper         Lead $NV = M$ | Mercury         Zinc         Copper         Lead $NPH$ | Mercury         Zinc         Copper         Lead         Cadn $NPBW$ $NPSW$ | Mercury         Zinc         Copper         Lead         Cadmium $NPBW$ | Mercury         Zinc         Copper         Lead         Cadmium $N_{HO}$ | Mercury         Zinc         Copper         Lead         Cadmium $NPW$ <td< td=""><td>Mercury         Zinc         Copper         Lead         Cadmium         Irc           <math>Mercury</math> <math>Mercury</math></td><td>Mercury         Zinc         Copper         Lead         Cadmium         Iron           <math>NY = 0</math> <math>NY = 0</math></td></td<> | Mercury         Zinc         Copper         Lead         Cadmium         Irc $Mercury$ | Mercury         Zinc         Copper         Lead         Cadmium         Iron $NY = 0$ |

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

effective alkalinity	er temperature (°C), pH,	ns, and extremes of wat	Mean, standard deviatio	Table 2:
24	107	6.7	18	
725	218	8.3	26	Summer
102	23	0.33	2.2	245
333	153	7.7	22	
6 L	- 56	5.9	11	
700	: 238	8.9	22.5	spring
16	38	0.56	2.0	•
320	107	7.6	15	
9	30	6.2	2.0	
750	161	8.1	9.0	AJULEL
117	30	0.45	2.1	
305	84	7.5	6.2 .	
MEAN STD. DEV. MAXIMUM	MEAN STD. DEV. MAXIMUM MINIMUM	MEAN STD. DEV. MAXIMUM MINIMUM	MEAN STD. DEV. MAXIMUM MINIMUM	Season
Specific Conductanc	Effective Alkalinity	PŦ	Water Temperature	

(CaCO3 in mg/l), and specific conductance ( $\mu$  mhos/cm @ 25°C) of unfiltered samples.

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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.

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.

.

		J/ (26	AMES RIVER 5N-22W-8-d	{ lc)		CRANE (26N-24)	CREEK I-29-cd)	JORDAN CREEK (29N-22W-27-db)				
Sample No	). •	30(W)	30(E) ·	Avg.	22(W)	22	22(E)	Avg.	51(W)	51(E)	Avg.	
Water Ten	ıp.	18.0	18.0	18.0	15.5	15.5	15.5	15.5	18.0	18.0	18.0	
pН		8.4	7.7	8.1	7.9	8.2	.7.8	8.0	7.1	7.3	7.2	
Spec. Cor	nd.	345	385	365	320	305	320	315	365	370	368	
Hg		<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	<]	17	19	18	
Cd		1 '	<]	0.8	2	1	2	2	<1 *	1	0.8	
Fe		<50	50	38	<50	<50	<50	<50	90	90	90	
Water Spe	ed	Swift	Swift		Slow	Swift	Şlow		Swift	Slow		
Stream De	pth (ft)	2.5-3	2.5-3		1-1.5	3-4	1-1.5		1.5-2	1-1.5	1-2	
Stream Wi	dth (ft)			60-70	1			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].

JAMES RIVER



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].

JAMES RIVER



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].

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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 and 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.

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

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> )	<pre>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.</pre>	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: (con	ntinued)	

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.
Cadmîum	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)

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#### CONCLUSIONS AND APPLICATIONS

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 original problem was to determine if significant amounts of the heavy metals mercury, zinc, copper, lead, cadmium, and iron do exist in the waters of the James River basin.

Main streams of the James River basin contain varying quantities of all metals sought in the research program. As a generalization, concentrations of 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 of this minute quantity 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 manmade pollution sources exist in the areas of exception. Relatively higher concentrations were not noted in the Springfield-Wilson Creek area.

Zinc contents in the stream waters range from  $\angle 1$  ppb to 80 ppb and 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  $\angle$  l 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 Greene County.

Specific conductance values range from 90 to 750 micromhos/ cm @ 25<sup>O</sup>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 newage 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 crosssection 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.

Finally, the metal content identified in the streams of the basin through three seasonal periods may be used as bench marks for future studies of the streams as the impact of increased population and industrialization affects the area.

PUBLICATIONS, REPORTS, PAPERS, TALKS PRESENTED

An abstract of the work has been published in the report of the Annual Meeting of the University of Missouri-Water Resources Research Center. At that same meeting, a 15-minute presentation was made before research workers from across the state, water administrators from universities and government agencies, and some members of the Citizens Advisory Committee for Water Resources. The title of the presentation was: "Heavy Metals in the Streams and Stream Sediments of the James River Basin, Missouri".

Two theses have been completed as a result of the project. The first listed was in part supported by OWRR funds, the second inherited some materials collected during the water study, but was funded for research from other sources. The theses are: (1) Heavy Metals in the Main Streams of the James River Basin, Missouri, by R. J. Lance, and (2) Heavy Metal Analysis of Stream Sediments in the James River Basin, Missouri, by W. H. Head.

### TRAINING ACCOMPLISHED

As a result of the partial funding of this research project, two master's degrees were completed with emphasis in water resources. A spin-off use of a post-doctorate student in sediment analysis also resulted from the study. Results of the research have been included as case histories in hydrogeology, geochemistry and in mineral exploration.

#### REFERENCES

- Beveridge, T. R., 1970, Geology of the Bassville quadrangle, Greene County, Missouri: Mo. Geol. Survey and Water Resources, Geol. Quad. Map Series No. 4, map with 35 page text.
- Brown, Eugene, Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: Chapter Al, Techniques of Water-Resources Investigations of the U.S. Geological Survey, Book 5, Laboratory Analysis, 16Cp.
- Clark, E. L., 1941, Geologic map of the Cassville quadrangle, Missouri: Mo. Geol. Survey and Water Resources, 2nd ser., one sheet.
- Clark, E. L., and Beveridge, T. R., 1952, Guidebook (of the sixteenth regional field conference of the Kansas Geological Society) for West-Central Missouri: Missouri Geol. Survey and Water Resources, Rept. of Inv. 13.
- Environmental Protection Agency, 1971, Methods for chemical analysis of water and wastes: E.P.A., Analytical Quality Control Laboratory, pp. 121-130.

\_\_\_\_\_, 1972, Water quality standards criteria digest - Mercury and heavy metals: E.P.A. August, 9p.

Feder, C. L., Skelton, John, Jeffrey, H. C., and Harvey, E. J., 1969, Water resources of the Joplin area, Missouri: Mo. Geol. Survey and Water Resources, Water Resources Rept. 24, 97p.

Federal Water Pollution Control Administration, 1968, Report of the committee on water quality criteria: F.W.P.C.A., April, 234p.

, 1969, James River-Wilson Creek study, Springfield, Mo.: F.W.P.C.A., vols I and II, June.

Fellows, L. D., 1963, Guidebook to solution phenomena in the Springfield metropolitan area, Greene County, Missouri: Mo. Geol. Survey and Water Resources, September, 30 p.

, 1970, Geology of the Galloway quadrangle, Greene County Missouri: Mo. Geol. Survey and Water Resources, Geol. Quad. Map Series No. 5, map with 15 page text.

Grohskopf, J. G., and McCracken, Earl, 1949, Insoluble residues of some Paleozoic formations of Missouri, their preparation, characteristics, and application: Mo. Geol. Survey, Rept. of Inv. 10, 39 p.

- Harvey, E. J., and Skelton, John, 1968, Hydrologic study of a waste disposal problem in a karst area at Springfield, Missouri: U.S. Geological Survey Professional Paper 600-C, pp. C217-C220.
- Head, W. J., 1973, Heavy metal analysis of stream sediments in the James River Basin, Missouri: Masters Thesis in preparation at Univ. of Missouri-Rolla, Rolla, Missouri.
- Hem, J. D., 1970, Study and interpretation of the chemical characteristics of natural waters: U.S. Geol. Survey Water-Supply Paper 1473, 2nd ed., 363 p.
- Howe, W. B., coordinator; Koenig, J. W., editor, 1961, The stratigraphic succession in Missouri: Mo. Geol Survey and Water Resources, 2nd ser., vol. 40, 185p.
- Kisvarsanyi, Eva B., compiler, 1965, Mineral resources and industry map of Missouri: Mol Geol Survey and Water Resources, one sheet.
- McCracken, Mary H., compiler, 1961, Geologic map of Missouri: Mo. Geol. Survey and Water Resources, one sheet.

, 1971, Structural features of Missouri: Mo. Geol Survey and Water Resources, Rept. of Inv. 49, 99p., one sheet.

- Miesch, A. T., 1970, Environmental geochemistry: Geochemical survey of Missouri (second six-month period, January-June, 1970); U.S. Geol. Survey open-file report, 60 p.
- Missouri Geological Survey and Water Resources, Unpublished outcrop and geologic maps of James River basin area.
- Proctor, Paul Dean, and Kisvarsanyi, Geza, Garrison, E., and Williams, Anita, 1973, Water qualtiy as related to possible heavy metal additions in surface and ground water in the Springfield and Joplin areas, Missouri: Mo. Water Resources Research Center, Univ. of Mo.-Rolla, Rolla, Missouri, 56p.
- Shepard, E. M., 1898, A report on Greene County: Mo. Bur. Geol. and Mines, vol. 12, pt. 1, sheet rept. 5, 245 p.
- U.S. Bureau of Census, 1970, U.S. census of population: 1970, Numbers of Inhabitants; final report PC(1)-A27 Missouri.
- U.S. Geological Survey and Missouri Geological Survey and Water Resources, 1967, Mineral and water resources of Missouri: Mo. Geol. Survey and Water Resources, vol. 43, ser. 2, 321 p.

U.S. Geological Survey, 1970, Mercury in the environment: U.S. Geol. Survey Professional Paper 713, 67 p.

, 1971, Water Resources data for Missouri: U.S. G.S., pt. 1, pp. 160-162.

U.S. Public Health Service, 1962, Drinking water standards, revised 1962: Public Health Service Pub. 956, 61 p.

, 1969, Manual for evaluating public drinking water supplies: Public Health Service Pub. 1820, 62 p.

Vineyard, J. D., and Fellows, L. D., 1967, Guidebook to the geology between Springfield and Branson, Missouri, emphasizing stratigraphy and cavern development: Mo. Geol Survey and Water Resources, Rept. of Inv. 37, 39 p.

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### 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 1. The General Land Office Survey System is used for township, range, section, quarter section, and quarterquarter 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.

Q.

Sample Location	Sea- son	Water Temp(°C)	Hq	Effective Alkalinity	» Specific Conductance	Meta Hg	l Value Zn	es (par Cu	rts per Pb	cd Cd	(
ן 29:ו-19ייים 17-bb	S S S S	7.5 13.5 22.0	7.7 7.6 7.6	67 77 167	280 260 305	<pre>^0.1 </pre>	21 10 55	4 – %	~~~ÿ	°5 °- −	190 35 5
2 29:1- 19:1-8- ac	ы SU SU	7.0 14.0 22.0	7.6 7.5 7.4	54 66 107	225 245 240	<0.1 <0.1 <0.1	21 <10 55	4 <mark>-</mark> 5 2	~~~ <b>%</b>	~ ~ ~ ~	240 25 22
3 2911-1814-6-ac	S SU	7.0 14.5 22.0	6.5 7.6 7.6	59 59 110	240 225 240	<0.1 <0.1 0.2	31 35 35	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	~-%	35 35 5
4 29¦l-18¦¦-5-ab	S Su	7.0 14.5 22.0	7.7 7.7	64 62 135	220 220 245	60.1 60.1	10 10 10	- <del>.</del> °	,	0 m m	50 <10 40
<b>5</b> 29N-18¼-12-ad	м SU	7.0 14.5 21.8	6.2 7.7 7.2	62 59 135	235 240 250	60.1 60.1	13 55 55	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	<u>ک</u> ک ک	<sup>5</sup> م	60 35 17
6 28N-18¼-23-ca	s SU	7.5 14.5 24.0	7.0 7.1 7.6	74 77 161	240 230 300	60.1 60.1	18 16 16	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	~~ ÿ	31 22 11
7 28N-18N-23-bd	su SU	8.5 14.5 21.0	7.8 7.3 7.3	77 77 167	280 265 270	6.1 60.1	21 <10 35	- <del>-</del> ~ %	~~~~	°°°,	33 25 11

Sample	Sea-	Water		Effective	Specific	Meta	1 Value	s (pai	rts pe	r billi	on)
Location	son	Temp(°C)	рН	Alkalinity	Conductance	Hg	Zn	Cu	Pb	Cd	Fe
	W	6.5	6.8	69	245	<0.1	13	1	<]	2	30
8 28N-13%-24-cb	S SU	14.5	7.8	66 144	230 295	<0.1	<10 35	1	<1 <2	3	<10 <2
•	• W	7.0	6.9	57	170	<0.1	13	2	<1	<1	17
9 27N-19W-12-ba	S	13.5	7.9	90	265	<0.1	10	<1	<1	2	<50
	SU	21.0	6./	138	280	0.2	35	<2	<2	<2	5
10	W	6.0	7.1	77	280	<0.1	27.	3	<]	<]	20
27N-191-1-ca	SU	14.5	7.7	151	300	<0.1	35	<2	<2	3	11
11	W	7.5	7.8	75	265	<0.1	13	2	<1	2	33
27N-19W-18-db	S SU	15.0 21.0	7.8	123 138	220 280	<0.1 <0.1	25 16	1 <2	<1 <2	1 <2	<50 5
·	1.1	7 5	7 0	*	075	-0.1	'i 10	2	.1	7	20
12	W S	16.0	7.8 8.1	116	275	<0.1	13	<1	<1 <1	2	30 <50
2/N-20W-18-CD	SU	24.0	7.7	138	280	0.2	55	<2	<2	<2	11
13	W	7.5	7.4	82	295	<0.1	<10	1	. <1	<1	20
26N-22W-1-bd	S SU	16.0	7.8 8.0	133 162	315 280	<0.1	10 16	<1 <2	<1	2 <2	<50 5
•		2010	0.0	TOL	200	0.1	1.0				5
14	W	2.5	65	67	230	<0.1	46 <10	5	41 •	3	16
23N-27W-3-cd	SU	19.5	7.6	146	270 -	0.3	16	<2	<2	<2	15

.

Sample	Sea-	Water		Effective	Specific	Meta	al Valu	es (pa	rts pe	r bill	ion)
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-27V-12-ca	S	14.5	8.3	72	290	<0.1	10	<1	<1	7	<10
	SU	21.0	7.7	135	255	0.2	35	<2	<2	<2	5
16	-11	4.0			275	<0.1	24	7	23	4	34
24N-27V-1-ab	S	14.0	7.5	69	285	<0.1	23	<]	<1	5	<10
241-271-1-00	SU	18.0	7.5	141	280	0.2	16	<2	<2	<2	<2
17	W	2.5			340	<0.1	10	3	<2	<2	38
24N-261-24-22	S	16.0	7.7	90	315	<0.1	<10	<]	<]	3	13
	SU	22.0	7.6	194	340	<0.1	16	<2	<2	<2	5
19	W	3.5			295	<0.1	10	5	<2	<2	37
24N-26U-24-ad	S	14.0	7.9	56	260	<0.1	10	<]	4	5	<10
2411-2011-24-00	SU	22.0	. 8.0	128	285	0.3	16	<2	. <2	<2	5
10	W	2.0			260	<0.1	<10	<2	10	2	21
19 22N 25U 5 co	S	15.0	8.0	90	300	<0.1	<10	4	2	3	<10
2511-2511-0-Ca	SU	20.0	7.5	167	330	0.1	<10	<2	<2	<2	5
20	W	2.5			255	<0.1	<10	3	<2	<2	25
2411-2411-30-da	S	15.5	8.2	87	235	<0.1	<10	<1	4	5	13
	SU	24.5	8.1	136	255	<0.1	16	<2	<2	<2	iĩ.
21	W	2.5			260	<0.1	10	2	<2	2	33
21 21 N. 21 J. J. do	S	13.0	7.9	95	315	<0.1	<10	<1	2	7	<10
2411-24W-17-0C	SU	18.5	7.3	197	375	0.3	35	<2	<2	<2	<2
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Sample	Sea-	Water		Effective	Specific	Meta	al Valu	ies (pa	rts pe	r bil	lion)
Location	son	Temp(°C)	рН	Alkalinity	Conductance	Hg	Zn	Cu	РЬ	Cd	Fe
22	W	6.5	7.3	82	240	<0.1	<10	<]	<]	<]	19
<b>2611-24</b> W-29-cd	S SU	15.5 21.0	8.0 7.8	135 167	315 315	<0.1 0.1	23 35	<1 <2	<1 <2	2 <2	<50 <2
23	W	4.0			340	<0.1	10	5	<2	<2	32
2311-2311-17-db	S SU	19.0	8.2	161		<0.1	20	<2	<2		8
24 24N 22U 7ch	W S	3.5 14.0	7.2	84	375 300	<0.1 <0.1	13 <10	9 <1	<2 <1	<2 <1	35 50
2411-23W-7-CD	SU	21.0	8.2	156		<0.1	38	<2	<2		8
25 25N-24W-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 25№-23₩-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
<b>27</b> 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

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Sample	Sea-	Water		Effective	Specific	Meta	al Valu	es (pa	rts ne	r bil	lion)
Location	son	Temp(°C)	рН	Alkalinity ·	Conductance	Hg	Zn	Cu	Pb	Cd	Fe
20	W	7.5	7.5	77	280	<0.1	<10	1	<1	<]	20
29 25N-23W-12-da	S SU	16.0 22.0	5.9 8.1	130 144	280 285	<0.1 0.1	<10 20	<1 <2	3 <2	6	<50 3
30	W	9.0	7.6	95 156	350	<0.1	12	1	<]	<]	20
26N-22W-3-dc	SU	25.0	7.7	176	575	<0.1	20	<2	<2	•	24
<b>31</b> 2611-2211-8-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
<b>34</b> 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	<] 1	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	er bill	lisr)
Location	son	Temp(°C)	рН	Alkalinity	Conductance	Hg	Zn	Cu	Pb	Cd	ře
26	W	8.0	6.7	136	465	<0.1	19	3	<]	<1	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	71 22
37	.M	7.5	8.1	62	230	<0.1	19	3	<]	<]	140
29N-20W-31-bb	S SU	22.0	7.9	128	260 275	<0.1 <0.1	20	<1 4	<1 <2	3	5
38 29N-21W-35-ab	W S SU	9.0 11.0 19.0	8.1 7.2 7.8	102 116 189	380 375 400	<0.1 <0.1 <0.1	19 15 20	3 <1 2	2 1 <2	<1 5	20 13 6
39 28N-21W-15-cc	W S SU	8.5 13.0 25.5	7.5 6.6 8.3	92 80 126	265 265 260	<0.1 <0.1 <0.1	<10 <10 , 20	1 <1 2	1 2 <2	<] 3	100 59 2
40 28N-21W-30-ac	W S SU	7.5 22.5 24.0	7.2 8.1 7.8	85 130 135	300 320 295	<0.1 <0.1 <0.1	12 13 20	3 4 5	1 1 <2	<1 2	46 <50 6
<b>41</b> 29N-22W-7-aa	W S SU	6.0 17.5 25.5	7.1 7.2 7.5	161 238 218	750 700 725	<0.1 <0.1 <0.1	37 20 80	8 1 8	- 1 1 <2	<1 2	110 60 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

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Sample Location	Sea-	Water		Effective	Specific Conductance	Metal Values (parts per billion)					
	son	Temp(°C)	рН	Alkalinity		Hg	Zn	Cu	Pb	Cd	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	₩ 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	<] ]	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	<] <]	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	1 <1	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

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Sample Location	Sea- son	Water Temp(°C)	рН	Effective Alkalinity	Specific Conductance	Metal Values (parts per billion)					
						Hg	Zn	Cu	РЬ	Cd	Fe
50 29N-22W-23-bc	W S SU	7.5	7.4	36	165	<0.1	45	8	<]	<1	253
51 29N-22W-27-db	W S SU	18.0	7.2	113	368	<0.1	64	18	18	1	90
52 29N-22W-28-bb	W S SU	17.5	6.8	180	565	<0.1	42	3	<]	1	90
53 29N-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	<] <]	<1 3	10 <10

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