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*Environmental Sciences*

## SELECTED TRACE METALS IN THE UPPER ST. JOHNS RIVER AND THEIR LAND USE RELATIONSHIPS

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*ABSTRACT: Iron, copper and zinc were monitored in the water, sediments, and 4 species of fish of the upper St. Johns River, Florida. Surface water concentrations of total iron commonly exceeded 300 ug/l, the standard established by the Florida Department of Environmental Regulation for waters intended for public consumption (Class I waters). Total iron levels in the upper St. Johns River are regulated by a series of interacting natural processes such as the iron-phosphate cycle, inputs from nonartesian groundwater or bank seepage, complexation with dissolved organic compounds, increased land runoff during periods of high flow, and resuspension of bottom sediments during periods of increased discharge or wind mixing. Groundwater inputs in the headwaters region due to agricultural irrigation practices, in addition to runoff and groundwater seepage into the drainage canals entering the river, have significantly increased its trace metal content. Elevated trace metal levels were also found in sediments and fish tissue in the river. The results of multiple regression analyses indicated that as the extent of urban activity increases in undeveloped watersheds of the upper St. Johns River, total copper and total zinc concentrations in the surface waters of the watershed can also be expected to increase.*

METAL CONCENTRATIONS have been shown to be increasing in many aquatic systems as a result of accelerated urban, agricultural, or industrial development (MacKereth, 1965; Shimp, Leland, and White, 1970; Collinson and Shimp, 1972; Pita and Hyne, 1975; Haith, 1976). Bedient et al. (1975), studying the upper St. Johns River Basin, Florida, emphasized that future research efforts should be aimed at gathering more information on the hydrological and ecological responses to changes in land use and vegetation.

The upper St. Johns River basin has undergone rapid agricultural

development and urbanization in recent years, which has affected the water quality and reduced the storage capacity of the river and marsh. Historical data indicate that levels of dissolved solids, trace metals and various mineral components have been gradually increasing (Mason and Belanger, 1979). The upper St. Johns River basin, however, represents a valuable resource to Brevard County due to its role as a focal point for recreation and fishing and as the drinking water source (Lake Washington) for South Brevard County. Careful watershed management practices appear to be needed for the protection of this resource.

In this study, iron, copper, and zinc were monitored in 4 species of fish, in the water and in the sediments of the upper St. Johns River in order to evaluate land use-water quality relationships. Additional objectives of the research included evaluations of the role of natural interacting processes in regulating surface water trace metal concentrations, the accumulation of trace metals in bottom sediments and fish tissue, the relationships between fish weight and total length and trace metal levels in the muscle, gills, and liver, and the relationship between volatile solids (organic matter) and trace metal concentrations in the sediments.

**DESCRIPTION OF STUDY AREA**—The St. Johns River emerges from a dense marsh in east-central Florida and flows 418 km northward to Jacksonville where it empties into the Atlantic Ocean. The river, the southern third of which is fresh water, flows through an extensive marsh floodplain and a number of shallow fresh water lakes, including Lakes Helen Blazes, Sawgrass, Washington, Winder and Poinsett, which are located in Brevard County (Fig. 1). The broad floodplains along both sides of the river are due to the flat topography and resulting slow drainage. The climate of the region is humid subtropical. The average annual temperature of the area is 22°C and the average annual rainfall is approximately 143.3 cm. More than 50% of the yearly precipitation falls from June through August as short term showers and thunderstorms, resulting in high flow rates in the summer and early fall. The flat topography and paucity of rainfall in the winter and spring, however, result in extremely slow flow rates during those months. Hydrologic considerations of the upper St. Johns River basin are discussed by McElroy (1977).

**METHODS**—Surface water samples from 42 stations in the upper St. Johns River in watersheds SJ-1 (headwater region above Lake Helen Blazes), SJ-2 (Lake Helen Blazes and Lake Sawgrass), SJ-3 (Lake Washington), and SJ-5 (Lake Poinsett) were periodically monitored for total iron, total copper, and total zinc from April through September, 1978 (Fig. 2). Samples were collected in acid-washed glass bottles at a depth of 0.3 m.

Analyses were also conducted on 3 samples from deep (artesian) wells near Lake Washington and on 1 nonartesian groundwater sample. Analytical procedures for determining total metal concentration were performed according to techniques described in *Standard Methods* using a Jarrel-Ash MVA atomic absorption spectrophotometer (A.P.H.A., 1975).



Fig. 1. St. Johns River basin.

Sediment cores were collected in plexiglass tubes (3.8 cm inner dia.) at 26 selected sites within each of the 4 watersheds. A one-gram portion of each air-dried sediment subsample was accurately weighed and transferred into a 125 ml florence flask for digestion. The sample was digested using the acid digestion procedure described by Chernoff (1975). The digested solution was cooled for 15 min and filtered to remove silicates and other insoluble material which could clog the atomizer of the atomic absorption unit. Per-

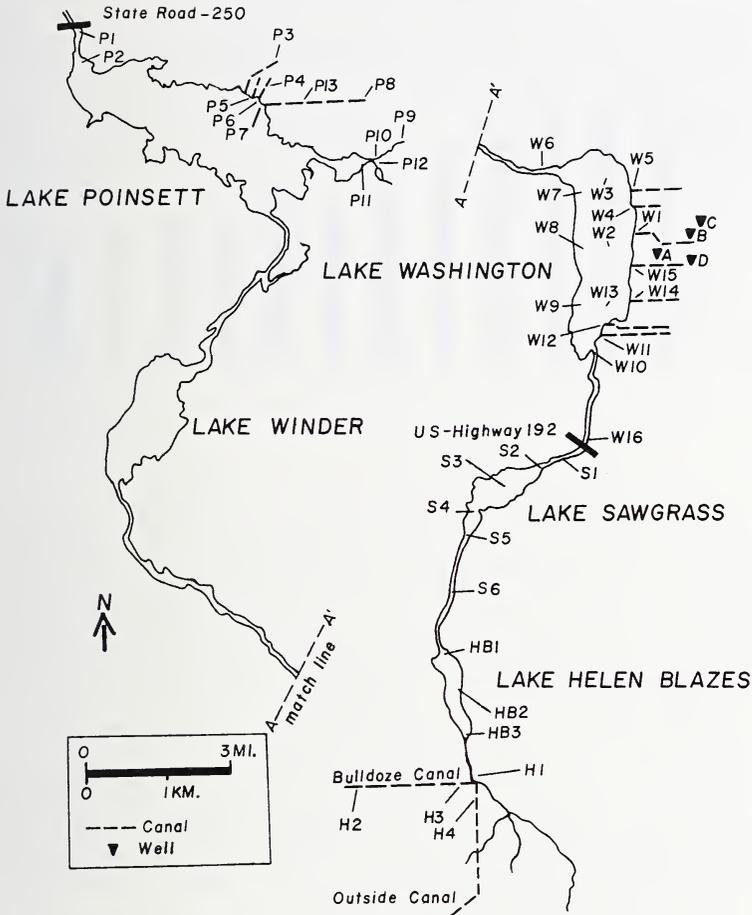


Fig. 2. Sampling stations.

cent organic composition of the sediments was estimated by measuring volatile solids lost upon ignition in a muffle furnace at  $550^{\circ} \pm 50^{\circ}\text{C}$  (A.P.H.A., 1975).

Forty-nine fish, including largemouth bass (*Micropterus salmoides*), bluegill (*Lepomis macrochirus*), speckled perch (*Pomoxis nigromaculatus*), and eastern chubsucker (*Erimyzon succetta*), were collected in February, 1978, using an electroshocking technique under the supervision of the Florida Game and Fresh Water Fish Commission. Fish were also collected during a fish kill in August 1978, caused by low dissolved oxygen levels. After collection, the fish were brought to the laboratory where weight and total length measurements were made. Axial muscle, gill tissue, and liver tissue were dissected from each fish and digested using the Chernoff (1975) procedure. Because complete digestion of fatty acids was not accomplished dur-

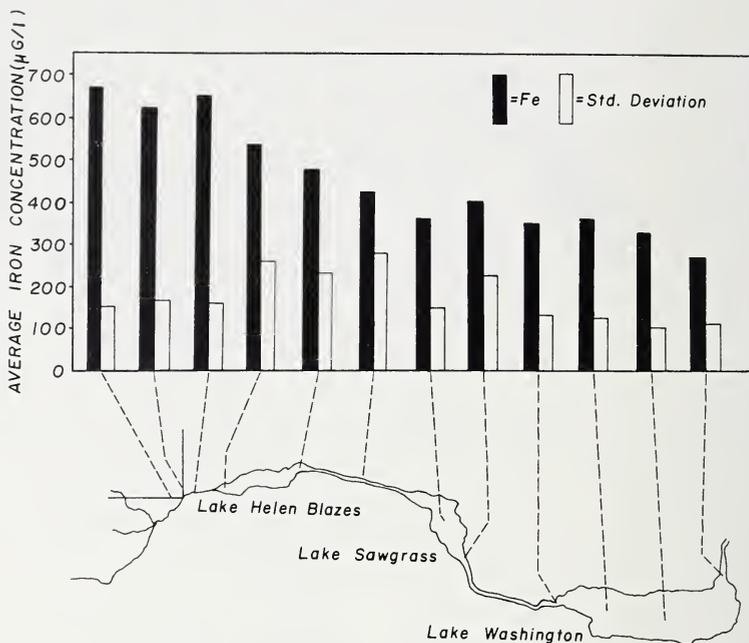


Fig. 3. Average surface water total iron concentrations at selected sites in the upper St. Johns River.

ing the digestion procedure, the fatty acids were separated in an organic phase using *n*-amyl alcohol to prevent clogging of the aspirator tube on the atomic absorption spectrophotometer. Water, sediment, and fish tissue samples, including spikes, were analyzed in duplicate or triplicate to evaluate precision and reproducibility of results.

**RESULTS AND DISCUSSION**—Mean surface water concentrations of total iron monitored at selected sites in the upper St. Johns River are in Fig. 3. Although total copper and total zinc were present in low concentrations in the surface waters, total iron levels frequently exceeded the state standard of 300 µg/l for Class I waters. Surface water concentrations of total copper varied from less than detection limits to 15 µg/l, while total zinc levels ranged from 8 to 58 µg/l throughout the basin. Highest average concentrations of total iron (> 600 µg/l) were measured in watershed SJ-1, the headwaters region of the upper St. Johns River, and decreased in a northward direction to Lake Washington. Groundwater inputs in the headwaters region, due largely to wells and irrigation practices on large cattle and citrus farms in the area, appear to be responsible for increased levels of total iron in the surface waters. The highest concentrations of total copper and total zinc, however, were measured in the surface waters of the Lake Washington and Lake Poinsett watersheds.

The impact of canal systems upon the surface water trace metal content

TABLE 1. Average trace metal concentrations in drainage canals of Lake Washington.

Sampling Site	Samples Analyzed	Metal Concentrations (ug/l)					
		Total Iron		Total Copper		Total Zinc	
		Average	Range	Average	Range	Average	Range
Canal W1	11	333	86-1140	3	ND-12	18	5-35
Canal W4	8	319	133- 570	7	ND-22	10	ND-17
Canal W5	9	330	228- 469	8	ND-22	13	4-18
Canal W11	8	397	177- 768	4	ND-22	13	4-18
Canal W12	8	386	141- 756	3	ND-22	13	4-20
Canal W14	8	322	149- 507	2	ND-12	19	ND-77
Canal W15	8	248	106- 424	6	ND-29	17	ND-34
Midlake	16	314	113- 613	2	ND-12	11	ND-18

ND = not detectable.

of the upper St. Johns River is well-pronounced within the Lake Washington watershed (SJ-3). Average surface water concentrations of trace metals monitored in the drainage canals of Lake Washington are compared to average mid-lake concentrations in Table 1. High levels of trace metals were also observed in the Lake Poinsett canal system. It appears that groundwater seepage and runoff into these canals, which to varying degrees drain residential and commercial areas, are responsible for adding increased levels of trace metals to the surface waters. Findings by Connor (1979) indicated high bank seepage rates in the canals of the upper St. Johns River and support this conclusion.

Results of analyses completed on a limited number of artesian and nonartesian groundwater samples indicate the total iron concentrations from deep (artesian) wells were generally lower than surface water levels. Nonartesian groundwater, however, is often very high in iron and consequently iron contributions from bank seepage may be very significant, particularly in the steeply sloping canals which can intercept nonartesian groundwater flow. Brown et al., (1962) reported iron concentrations as high as 4000 ug/l in nonartesian groundwater samples from the area. Similar results were found during this investigation as an iron concentration of 4550 ug/l was measured in a 7.6 m nonartesian well near Lake Washington.

In addition to groundwater inputs, levels of total iron in the surface waters also appear to be regulated by complex interactions of naturally occurring processes. Although the lakes in the upper St. Johns River are too shallow to undergo stable stratification and frequent oxygen depletion, the results of laboratory and field experimentation by Goolsby and McPherson (1970) indicate that iron-phosphate cycle interactions could dominate under conditions of low oxygen and pH. Dissolved organic compounds, predominantly fulvic acids characteristic of the highly colored waters of the upper St. Johns River, are responsible for keeping metallic ions in solution through complexation reactions.

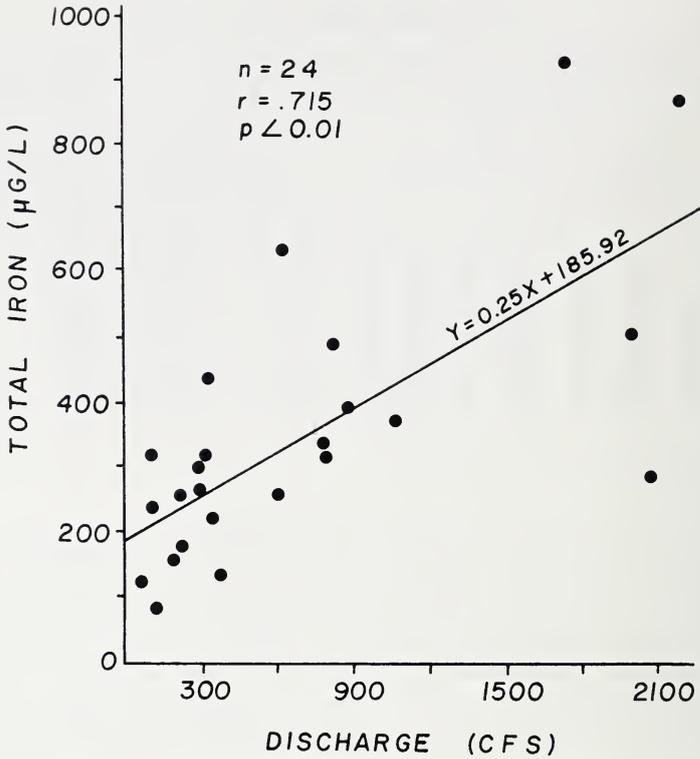


Fig. 4. Total iron concentrations in surface waters of upper St. Johns River as a function of discharge at gaging stations near Melbourne and Cocoa, Florida.

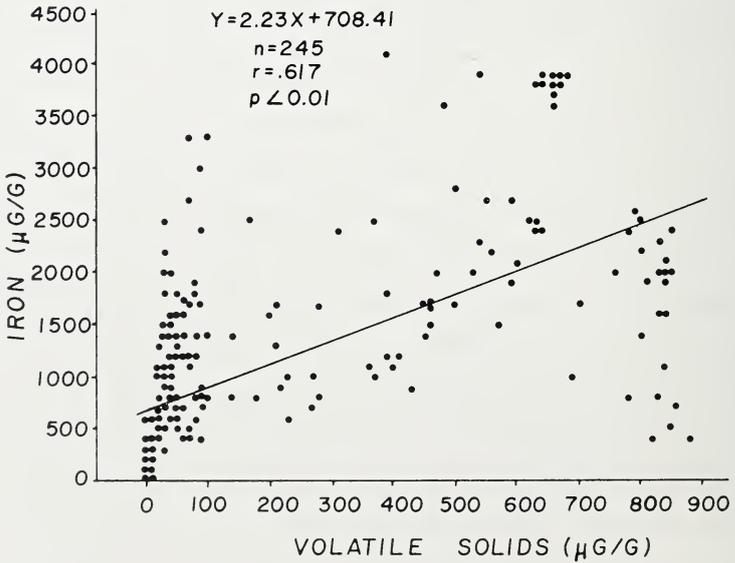


Fig. 5. Relationship of iron to sediment volatile solids.

Increased turbulence, caused by wind/wave action, outboard motors, or increased flow, may also be responsible for increasing total metal concentrations in the surface waters as a result of sediment disturbance and resuspension in the overlying water column. Using data collected by the United States Geological Survey (1976) for gaging stations located on the St. Johns River at US Highway 192 near Melbourne and State Road 520 near Cocoa, the relationship between discharge and total iron concentrations was verified. These data, shown graphically in Fig. 4, were highly significant ( $p < 0.01$ ) and demonstrate that total iron concentrations can be expected to increase linearly as a function of increasing discharge. Because total copper and total zinc have not been monitored routinely prior to this study, no attempt was made to correlate either of these variables with discharge.

The sediments of the upper St. Johns River vary in composition from sandy soils to organic-muck soils. Sandy sediments generally contained less than 10% volatile solids, whereas organic soils consisted of as much as 86% volatile solids. In these sediments, copper concentrations varied from less than detection limits to 25.1  $\mu\text{g/g}$ , while zinc levels ranged from 1.2 to 212.2  $\mu\text{g/g}$ . Iron reached a maximum concentration of 4090  $\mu\text{g/g}$  at the mid-lake station in Lake Washington, where organic-muck sediments were encountered.

Linear regression analyses were performed to determine whether sediment levels of iron, copper, and zinc were correlated with organic matter (volatile solids). These results, shown in Figs. 5 through 7, demonstrate that as the volatile solids content of the sediment increases, the concentrations of trace metals can also be expected to increase. These results suggest that organic and humic substances deposited in marsh sediments during deposition and decomposition of vegetation complex with metal ions, thus the accumulation of metals in the sediments.

Mean concentrations of iron, copper, and zinc in fish from the upper St. Johns River are in Table 2. These results indicate that trace metals are selectively concentrated within fish liver, while lower concentrations are found in the gills and the lowest levels are found in muscle. Exceptions to this trend were higher average copper and zinc concentrations in the gills of speckled perch and bluegill, respectively.

Linear regression analyses were performed on the data to evaluate the relationships between fish weight and total length and corresponding trace metal tissue concentrations. Because only 3 speckled perch and eastern chubsucker were analyzed, statistical tests were not performed on these data. Results of these tests indicated that iron accumulates within the liver of largemouth bass as a function of increasing body length. The regression, improved by using a coefficient of condition which incorporates total length and weight measurements into one variable, suggests that largemouth bass accumulate iron through time, with longer, heavier fish containing higher levels of iron in the liver. This relationship is shown in Fig. 8 and is expressed by the following equation:

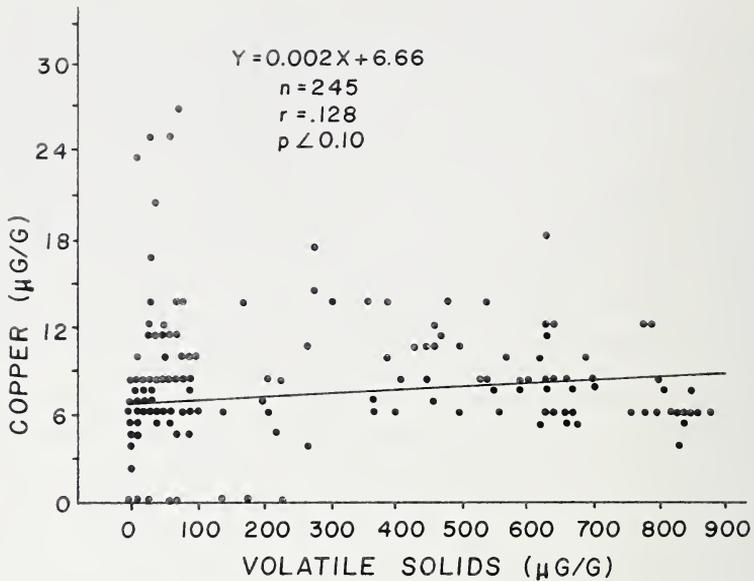


Fig. 6. Relationship of copper to sediment volatile solids.

$$\text{Liver Iron Concentration (ug/g)} = 480.8 (\text{Coefficient of Condition}) - 327.3 \quad (1)$$

where

$$\text{Coefficient of Condition} = \frac{\text{Fish Weight (grams)} \times 10^5}{\text{Fish Total Length (mm)}^3} \quad (2)$$

A series of negative correlation coefficients were obtained when copper and zinc concentrations in the tissues of bluegill and largemouth bass were compared to body length and weight. The negative correlations suggest that, as these fish age, more efficient means are available for excreting copper and zinc from the body, or that avoidance behavior to higher concentrations is learned.

Water quality-land use relationships were statistically evaluated by multiple regression techniques in order to identify nonpoint sources of variability in surface water levels of trace metals. Stepwise multiple regression techniques described by Haith (1976) for the study of land use and nonpoint source impacts on water quality were used in this investigation. Land use percentages for the 4 watersheds of the upper St. Johns River sampled within in this study are in Table 3. Following an arcsine transformation of the land use percentages to prevent the variance of a binomial distribution for being a function of the mean, correlations between watershed land use and trace metal levels were calculated. These results, listed in Table 4, demonstrated that although total copper and total zinc were highly cor-

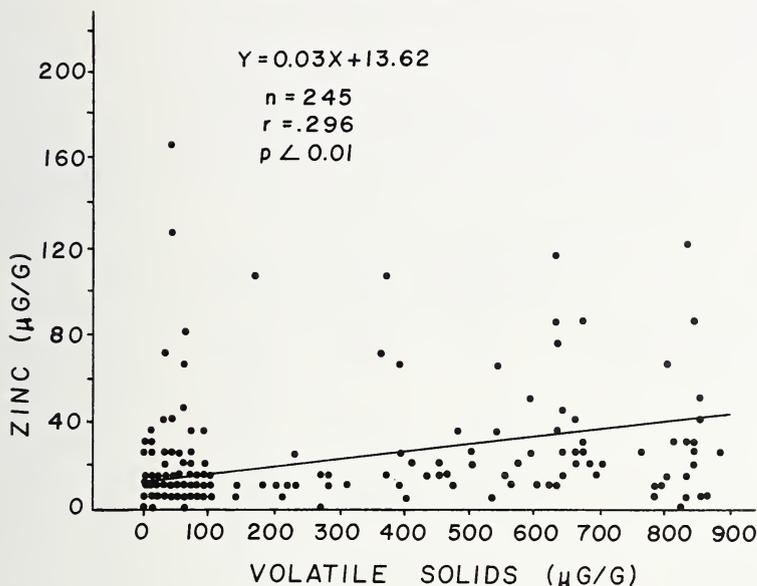


Fig. 7. Relationship of zinc to sediment volatile solids.

related to several land uses, total iron exhibited no significant correlations. Total copper was most highly correlated with residential land use, while total zinc was most strongly correlated with commercial-institutional-industrial uses.

The multiple regression equations generated to predict the relationships between land uses and surface water levels of total copper and total zinc within watersheds SJ-1, SJ-2, SJ-3, and SJ-5 are in Table 5. The final equation for total copper (step 2) explained 99.68% ( $r^2 = 0.9968$ ) of the observed variation, with residential areas (Res) accounting for approximately 92% of this variation and marsh accounting for the remainder. Transportation (Trans) and commercial-institutional-industrial areas (C-I-I) explained 98.62% of the observed variation in total zinc levels with C-I-I accounting for nearly 96% of the variation. Because of collinearities present in the land uses of the 4 watersheds (e.g., urban uses tend to increase while agricultural uses proportionately decrease), an equation using percent C-I-I land use accounted for 95.60% of the observed variation in average total zinc, while an equation employing percent residential land use was nearly as suitable, explaining 95.26% of the variation. Although present concentrations of total copper and total zinc in the surface waters of the upper St. Johns River are low, the regression results indicate that as the extent of human utilization and urbanization of agricultural and undeveloped watersheds increases and natural land cover decreases, total copper and zinc concentrations in the surface waters can also be expected to increase.

TABLE 2. Average trace metal concentrations in fish tissue.

Species	Number Analyzed	Metal	Tissue	Concentration (ug/g, wet weight)	
				Mean	Range
Largemouth Bass ( <i>Micropterus salmoides</i> )	28	Iron	Muscle	11.8	ND- 58.4
			Gill	55.3	17.4-270.3
			Liver	207.8	47.5-381.0
	28	Copper	Muscle	2.9	ND- 13.6
			Gill	7.3	ND- 39.7
			Liver	11.2	2.7- 44.1
	28	Zinc	Muscle	9.2	ND-131.3
			Gill	24.3	7.9- 50.6
			Liver	37.6	ND-116.2
Speckled Perch ( <i>Pomoxis nigromaculatus</i> )	3	Iron	Muscle	3.2	1.8- 5.1
			Gill	24.8	ND- 43.9
			Liver	86.2	23.6-165.8
	3	Copper	Muscle	3.6	1.3- 4.7
			Gill	11.5	2.3- 16.3
			Liver	10.7	10.0- 11.0
	3	Zinc	Muscle	8.6	0.6- 16.4
			Gill	23.3	15.7- 30.2
			Liver	37.0	21.6- 67.3
Bluegill ( <i>Lepomis machrochirus</i> )	12	Iron	Muscle	8.0	ND- 25.2
			Gill	55.3	13.0-223.7
			Liver	126.0	20.1-232.5
	12	Copper	Muscle	3.6	ND- 10.3
			Gill	10.3	1.1- 49.4
			Liver	29.1	3.9-182.1
	12	Zinc	Muscle	15.2	ND-104.3
			Gill	43.3	15.7-128.0
			Liver	42.8	11.7- 87.8
Eastern Chubsucker ( <i>Erimyzon succetta</i> )	3	Iron	Muscle	2.2	ND- 3.7
			Gill	35.9	ND- 80.2
			Liver	114.4	91.6-130.3
	3	Copper	Muscle	1.9	1.3- 2.5
			Gill	4.1	2.3- 5.0
			Liver	11.7	9.3- 14.8
	3	Zinc	Muscle	7.8	5.4- 12.3
			Gill	27.3	26.2- 29.4
			Liver	30.3	22.5- 37.2

ND = not detectable.

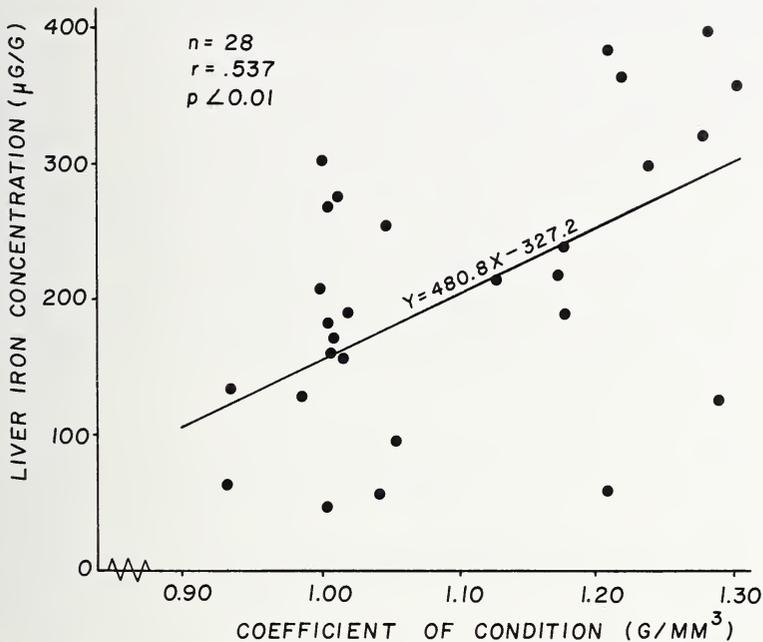


Fig. 8. Iron concentrations in the liver of largemouth bass as a function of coefficients of condition.

**SUMMARY AND CONCLUSION**—Findings from our research indicate that:

1. Although total copper and total zinc were present in low concentrations in the surface waters of the upper St. Johns River, total iron frequently occurs in concentrations exceeding the state standard of 300  $\mu\text{g/l}$  set by the Florida Department of Environmental Regulation for Class I waters.

2. Levels of total iron in the surface waters of the upper St. Johns River appear to be regulated by resuspension of bottom sediments caused by increased discharge and resulting turbulence.

3. Groundwater inputs from springs, wells, or upward seepage through the lake and canal sediments may also influence the trace metal content of the surface waters. Because total iron concentrations in nonartesian groundwater are high, significant contributions of iron is likely added to the surface waters from nonartesian or bank seepage.

4. Average surface water total iron concentrations were highest in the headwaters region of the river above Lake Helen Blazes, decreased in a northward direction to Lake Washington, and increased to Lake Poinsett. Highest average concentrations of total copper and total zinc were measured in the surface waters of Lake Poinsett and Lake Washington, where groundwater seepage and land runoff into the drainage canals add elevated levels of trace metals into the mainstem of the river. Groundwater inputs, particularly from nonartesian wells, are thought to be responsible for increasing

TABLE 3. Watershed land uses of upper St. Johns River Basin (from Brevard County Zoning and Planning Commission).

SJ-1	Percent Land Use Within Watershed			Land Use Category
	SJ-2	SJ-3	SJ-5	
0.07	0.02	1.40	7.03	Residential
		0.33	2.40	Comm-Instit-Industrial
60.05	35.32	38.44	13.50	Agriculture
37.74	64.44	45.57	46.54	Marsh
0.11		13.66	28.90	Vacant
0.03	0.22	0.60	1.63	Transportation

TABLE 4. Significant correlations between land use and water quality parameters.

Land Use	Total Iron	Total Copper	Total Zinc
Residential	—	0.958*	0.976*
Agricultural	—	—	—
Marsh	—	—	—
Vacant	—	0.939*	0.913*
Transportation	—	—	0.889*
Commercial- Institutional- Industrial	—	0.945*	0.978**

\*Significant at 0.05 confidence level.

\*\*Significant at 0.01 confidence level.

TABLE 5. Multiple regression equations for explaining water quality-land use relationships.

Step	Equation	Explained Variance $r^2$	F-value	Significance Level
<b>TOTAL COPPER:</b>				
1	Copper = $0.56 + 0.36$ (Arcsine % Res)	0.9185	22.55	0.05
2	Copper = $6.04 + 0.32$ (Arcsine % Res) - $0.12$ (Arcsine % Marsh)	0.9968	154.39	0.10
<b>TOTAL ZINC:</b>				
1	Zinc = $11.20 + 0.84$ (Arcsine % C-I-I)	0.9560	43.41	0.025
2	Zinc = $12.84 + 1.34$ (Arcsine % C-I-I) - $0.83$ (Arcsine % Trans)	0.9862	35.72	—
% C-I-I deleted from equation:				
	Zinc = $10.55 + 0.52$ (Arcsine % Res)	0.9526	40.20	0.025

surface water concentrations of total iron in the headwater region of the upper St. Johns River.

5. Higher levels of iron ( $r = .617$ ;  $p < 0.01$ ), copper ( $r = .128$ ;  $p < 0.10$ ), and zinc ( $r = .296$ ;  $p < 0.01$ ), were found in sediments containing higher percentages of organic matter (volatile solids), suggesting that humic substances deposited in these sediments during decomposition of vegetation complex with metal ions forming a sink for the metals.

6. Analysis of iron, copper, and zinc in the tissues of largemouth bass, speckled perch, eastern chubsucker, and bluegill indicated that these metals are concentrated in the fish liver, while lower concentrations are found in the gill and lowest levels are found in muscle tissue. Exceptions to this trend were the gills of speckled perch and bluegill where higher average copper and zinc concentrations occurred, respectively. Statistical results suggested that iron accumulates in the liver of largemouth bass through time and that more efficient means of excreting copper and zinc are available to largemouth bass and bluegill as the fish ages.

7. Multiple regression techniques used to evaluate water quality-land use relationships demonstrated that levels of total copper and total zinc were highly correlated to land uses associated with urban activities. Average total copper concentrations were best predicted by an equation using percent residential land use, while total zinc levels were best predicted using percent commercial-institutional-industrial use or one using percent residential use. These results indicate that as the extent of human utilization of undeveloped watersheds increases and natural land cover decreases, total copper and total zinc concentrations can also be expected to increase in the surface waters of the upper St. Johns River.

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