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Region 2
Contaminants Program

ENVIRONMENTAL CONTAMINANTS IN SEDIMENT AND FISH OF MINERAL CREEK AND THE MIDDLE GILA RIVER, ARIZONA

by

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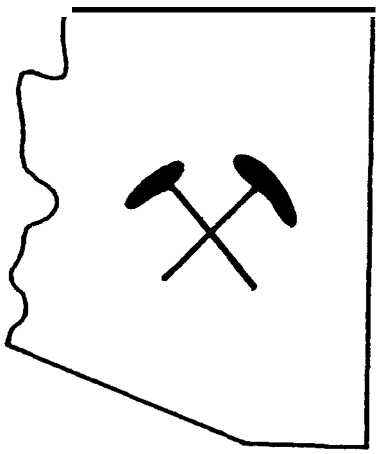

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ABSTRACT

The lower reaches of Mineral Creek, a tributary to the Gila River in Pinal County, Arizona, were thought to be polluted by discharges from ASARCO Ray Mine located adjacent to the creek. Mineral Creek was sampled in 1993 to assess habitat quality and ascertain fish populations and diversity. Sample sites upstream of the mine were characterized by high species diversity (n=5) and abundance. In stark contrast, no fish were captured in the downstream sites.

Mineral Creek, downstream of Ray Mine, and four sites on the Gila River were sampled again in October 1995. Roth sediment and fish were collected and analyzed for trace elements. Species diversity and abundance had improved significantly in Mineral Creek from 1993 to 1995. Four species of fish were found in Mineral Creek downstream of the mine in 1995. Copper concentrations were elevated in sediment and fish. Copper in sediment from Mineral Creek was 40-times the state mean (30 $\mu g/g$) and copper concentrations in fish from Mineral Creek far exceeded the maximum level reported from all 117 stations sampled nationwide. Lead and zinc in sediment from Mineral Creek were more than 3-and-4-times the state mean (23.4 and 62.1 $\mu g/g$, respectively); however, lead was detected only in a small proportion in fish. Lead concentrations in fish from four sites on the Gila River exceeded the threshold level that could potentially harm fish reproduction and survival.

Despite continuing high concentrations of copper, lead, and zinc, in sediment and some fish samples, the overall ecology of Mineral Creek improved from 1993 to 1995. Cleanup efforts by the mine improved ecological conditions of Mineral Creek, and by 1995, four species of fish were present in the area that was nearly devoid of fish only two years earlier.

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INTRODUCTION

Mineral Creek, a tributary to the Gila River in Pinal County, Arizona, may have polluted the Gila River during the 1980s and early 1990s by distributing high levels of metals within the watercourse (Stephenson and Ohmart 1974). The lower reaches of Mineral Creek were thought to contain high loads of contaminants possibly from ASARCO'S Ray Copper Mine (Ray Mine) located adjacent to Mineral Creek (Figure 1). Numerous complaints were received by the Arizona Game and Fish Department (AGFD), Arizona Department of Environmental Quality (ADEQ), and the U.S. Fish and Wildlife Service (FWS) regarding discolored water and lack of fish in portions of Mineral Creek downstream from the mine.

AGFD and FWS personnel completed extensive sampling of fish populations in Mineral Creek in July 1993 to assess potential aquatic system impacts of Ray Mine. Four 305-meter reaches of stream that contained representative portions of riffle, run, and pool habitats were identified and sampled for fish density and diversity. Two reaches were sampled upstream of Ray Mine, and two reaches were sampled downstream of the mine using a Coffelt Mark 10 backpack electrofisher. Five species of fish were collected, weighed, measured, then released, from the reaches upstream of Ray Mine. The five species collected included two native species, longfin dace (*Agosia chrysogaster*) and chub (*Gila* spp.), and non-native fish including, fathead minnow (*Pimephales promelas*), green sunfish (*Lepomis cyanellus*), mosquitofish (*Gambusia affinis*). No fish were collected downstream of the mine, although one individual was observed.

Fish populations present in the sites upstream of Ray Mine were characterized by high species diversity and abundance. Aquatic insects, both larvae and adults, were also abundant on the water surface and in the water column at the upstream reaches, but were nearly absent from downstream sampling sites. The significant decrease in fish and aquatic insect populations and subsequent decline in species diversity indicated that biota in the downstream portion of the creek may soon be extirpated due to low habitat quality and high metal content within the system.

Recent (1993) data from EPA test wells on the Ray Mine site indicated that pregnant leach solution (PLS) ponds were leaking water that contained sulfuric acid, copper, and other elements, and that PLS waters were resurfacing at three locations in Mineral Creek. However, there was no direct chemical evidence of metal contamination in biota of Mineral Creek or the Gila River immediately downstream from its confluence with Mineral Creek.

The Gila River and its tributaries represent major lotic waters and provide important riparian habitat for wildlife in southeastern Arizona, including the federally endangered southwestern willow flycatcher (*Empidonax traillii extimus*). Other avian species supported by this important habitat include yellow-billed cuckoo (*Coccyzus americanus*), common snipe (*Gallinago gallinago*), belted kingfisher (*Ceryle alcyon*), and various warblers.

The purpose of this study was to revisit the area, collect sediment and fish samples for analyses, isolate the source of contaminants, and detect potential aquatic ecosystem impacts.

STUDY AREA

The middle Gila River is defined as that portion of the river from Coolidge Dam downstream to Ashurst-Hayden Dam (Figure 1). Potential sources of pollution along this section of the river include mining, municipal discharges and agricultural runoff. Numerous mining operations are scattered throughout the middle Gila River. Cyprus Copper Company Mine (formerly Inspiration Consolidated Copper Company Mine) at Dripping Springs Wash is the first major mine below Coolidge Dam (Figure 1). A second large mining operation, Ray Mine, is located on Mineral Creek. Also, two large copper smelters are situated downriver from Winkleman. Toxic substances have been introduced from the mines into the river by direct discharge into tributaries and by runoff of mining wastes (Cox 1976) and by leaching of PLS ponds.

Five collection sites were selected on the Gila River and one in Mineral Creek approximately seven kilometers downstream of Ray Mine. Mineral Creek is a tributary of the Gila River located between Riverside and Cochran, Arizona. We selected one site (Riverside) on the Gila River upstream of its confluence with Mineral Creek, and four sites on the river downstream of Mineral Creek; Ripsey Wash, Cochran, Donnelly Wash, and Ashurst-Hayden Dam (Figure 1).

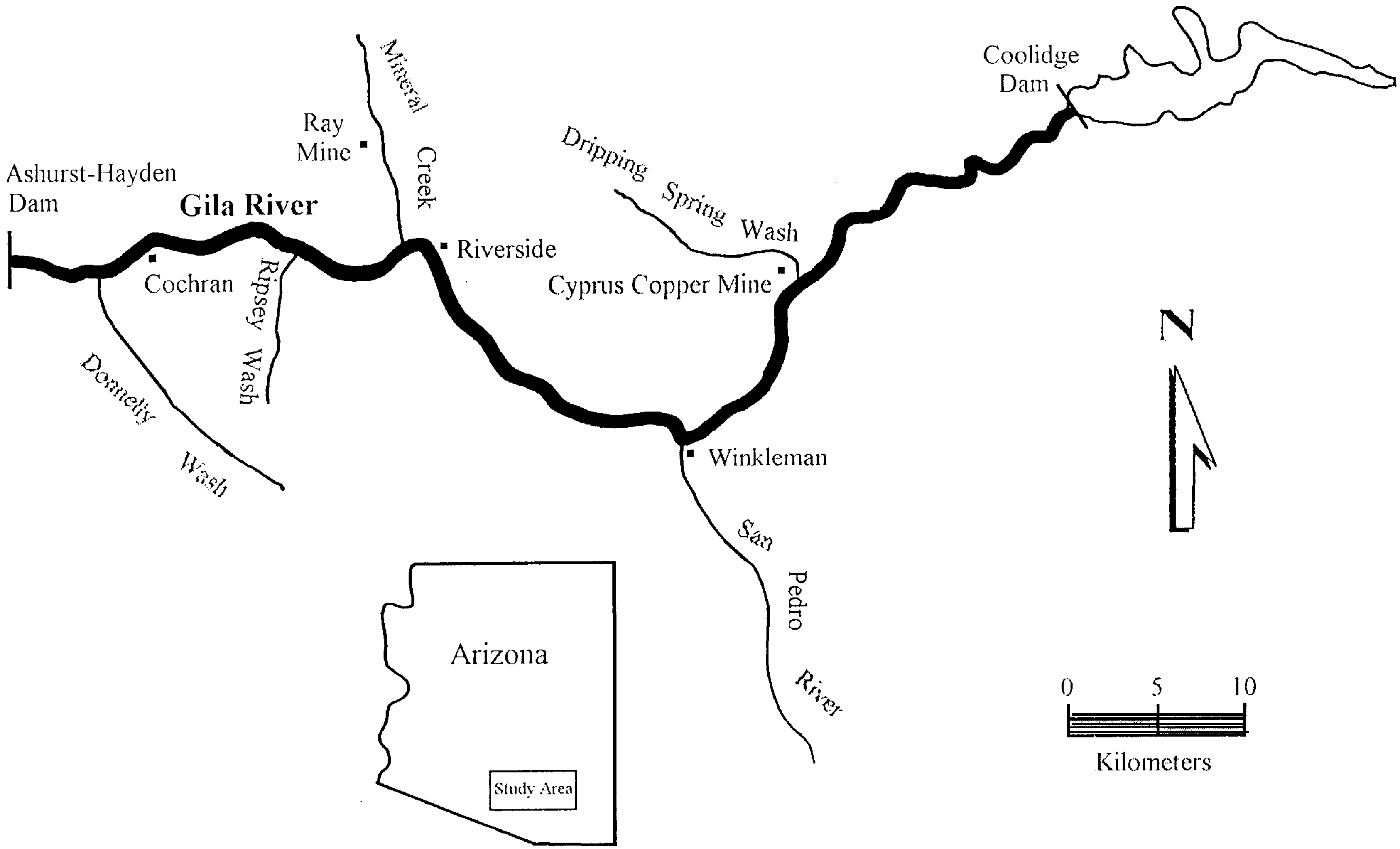

Figure 1. Area of study within the middle **Gila** River, **Pinal** County, Arizona, 1993-95.

METHODS

Sample collections:

Sediment was collected from four of six sites and fish were collected from all sites, except Ripsey Wash, during October 1995. All samples were analyzed for trace elements. Five sediment subsamples were taken at each site using a stainless steel spoon and pan, then homogenized into a single composite sample per site. Approximately the top 10 cm of sediment was collected for each subsample. Spoonful-aliquots of the homogenous composite mixture were placed in an acid-rinsed glass jar, weighed, sealed with a teflon-lined lid and placed on wet ice until the sample could be transferred to a commercial freezer and stored until they were shipped for trace element analyses. Black bullhead (*Ictalurus melas*), desert sucker (*Pantosteus clarki*), green sunfish, longfin dace, and mosquitofish were collected using a Smith-Root Model 12 backpack electrofisher. Fish were weighed, measured, and composited by species (n = 3-70) at each site. Whole body composite samples were wrapped in aluminum foil and placed on wet ice until they were transferred to a commercial freezer and stored until they were shipped for trace element analyses.

Chemical analysis:

Sediment and whole body fish were analyzed for aluminum, arsenic, barium, beryllium, boron, cadmium, chromium, copper, iron, lead, magnesium, manganese, mercury, molybdenum, nickel, selenium, strontium, vanadium, and zinc at Hazleton Environmental Services, Inc., Madison, Wisconsin. Mercury concentrations were quantified by cold vapor atomic absorption. Arsenic and selenium were analyzed by hydride generation atomic absorption spectrophotometry. All other elements were quantified by using inductively coupled plasma emission spectroscopy following **preconcentration** to lower detection limits. Trace element concentrations in sediment (Table 1) are reported in **μg/g** (parts per million) dry weight while element concentrations in fish (Table 2) are reported in **μg/g** wet weight unless otherwise specified. Percent moisture is listed in Table 2 to facilitate wet weight to dry weight conversions. Wet weight values can be converted to dry weight equivalents by dividing the wet weight values by one minus percent moisture. This is illustrated in the following equation:

$$\text{Dry weight} = \frac{\text{wet weight}}{1 - \text{percent moisture}}$$

Statewide background data on metals in Arizona soils was obtained by the U. S. Geological Survey (USGS) during a **14-year** period from 1961 to 1975 (Boemgen and Shacklette 1981). They analyzed 47 soil samples from various locations across the state to determine the concentration of selected metals. In order to compare our sediment data with USGS data, we will refer to the Arizona background level as the mean $\pm$ two standard deviations. Because only one composite sample was collected at Mineral Creek and each **Gila** River site, statistical comparisons with background levels are not possible on a site-by-site basis. If an element concentration exceeded the statewide mean plus two standard deviations, the concentration was considered substantially higher than the mean.

Whenever possible, element concentrations in fish were compared with those reported in the National Contaminant Biomonitoring Program **(NCBP)** for fish collected in 19761984 from 117 stations nationwide (Schmitt and Brumbaugh 1990). Concentrations of an element were considered elevated when they exceeded the 85th percentile of the nationwide geometric mean. The 85th percentile was not based on toxicity hazard to fish, but provided a frame of reference to identify element concentrations of potential concern.

RESULTS AND DISCUSSION

Trace Elements in Sediment:

Nineteen trace elements were detected in sediment samples (Table 1). Most elements were within Arizona background levels in soils (Boerngen and Shacklette 1981). The striking exceptions were copper, lead, and zinc. Copper was present at significantly higher concentrations than the background level in sediments from three of four sites. The highest copper concentration, 1245 µg/g dry weight, was present in Mineral Creek sediment and was 40-times the state mean of 30 µg/g . Residues may be declining, however, as sediment collected in 1991-92 from Mineral Creek contained 2660 µg/g dry weight copper (Ring and Raker 1995). Lead and zinc were present at substantially higher than background levels in sediments only from the Mineral Creek site. Lead in sediment from Mineral Creek was 72.37 µg/g; more than 3-times the state mean of 23.4 µg/g. The lead concentration in sediment from Mineral Creek in 1991-92 was 19.3 µg/g (Ring and Raker 1995), a concentration well below that found in this study. Zinc in Mineral Creek sediment (281.17 µg/g) was more than 4-times the state mean of 62.1 µg/g. Zinc residues have not declined as the zinc concentration in sediment from Mineral Creek in 1991-92 was 200.3 µg/g (Ring and Raker 1995). Arsenic was slightly elevated (17.97 µg/g) only at the Mineral Creek site. Although most element concentrations in sediment were within the background range, fourteen of nineteen elements were highest in sediments from Mineral Creek.

Trace Elements in Fish:

Thirteen trace elements recovered in fish tissues are presented in Table 2. NCBP data are available for seven elements: arsenic, cadmium, copper, lead, mercury, selenium, and zinc (Schmitt and Brumbaugh 1990).

Arsenic was detected in most fish samples with concentrations ranging from <0.05 to 1.11 μg/g wet weight (Table 2). Arsenic in six of thirteen fish samples exceeded the NCBP 85th percentile of 0.27 μg/g wet weight (Schmitt and Brumbaugh 1990). Walsh et al. (1977) considered arsenic concentrations >0.5 μg/g wet weight a level that could harm fish. The Riverside, Cochran, and Donnelly Wash sites contained fish with arsenic concentrations above this potentially harmful threshold.

Cadmium was recovered in 54% of the samples with concentrations ranging from <0.06 to 0.42 μg/g wet weight (Table 2). Of those detected, all exceeded the NCBP 85th percentile of 0.05 μg/g (Schmitt and Brumbaugh 1990). However, the lower limit of quantification for cadmium was 0.06 μg/g wet weight and the NCBP 85th percentile was 0.05 μg/g. Only the desert sucker sample from Mineral Creek (0.42 μg/g) approached the 0.5 μg/g wet weight threshold considered harmful to fish and predators (Walsh et al. 1977).

Copper was detected in all fish samples, and concentrations ranged from 0.43 to 38.40 μg/g wet weight (Table 2). Eighty-five percent (85%) of the samples exceeded the NCBP 85th percentile of 1.0 μg/g (Schmitt and Brumbaugh 1990). The highest copper concentration was in fish from Mineral Creek with a mean of 20.2 μg/g. In comparison, the means from other sites were 3.0 μg/g (Riverside), 4.57 μg/g (Cochran), 5.29 μg/g (Donnelly Wash), and 2.52 μg/g (Ashurst-Hayden Dam). The mean copper concentration in fish from the Gila River at Donnelly Wash from collections in 1991-92 were 2.32 μg/g (Ring and Baker 1995). Copper levels in fish from Mineral Creek were higher than the maximum level reported in all 117 stations nationwide (Schmitt and Brumbaugh 1990). Effects of high concentrations of copper on fish are not well established; however, there is evidence that fish fed a high copper diet can experience toxicity (Woodward et al. 1994). Copper can combine with other contaminants such as ammonia, mercury, and zinc to produce an additive toxic effect on fish (Herbert and Vandyke 1964, Rompala et al. 1984).

Lead was recovered in four of thirteen samples with concentrations that ranged from 0.54 to 2.34 μg/g wet weight, all of which exceeded the NCBP 85th percentile of 0.22 μg/g (Schmitt and Brumbaugh 1990). Lead was not detected in fish from Mineral Creek and Ashurst-Hayden Dam sites. Lead is highly toxic to aquatic organisms, especially fish (Rompala et al. 1984). The biological effects of sublethal concentrations of lead include delayed embryonic development, suppressed reproduction, inhibition of growth, increased mucous formation, neurological problems, enzyme inhibition, and kidney disfunction (Rompala et al. 1984, Leland and Kuwabara 1985). Lead concentrations in whole body fish exceeding 0.5 μg/g wet weight have the potential to harm fish reproduction and survival (Walsh et al. 1977). Composite samples of fish from Riverside, Cochran, Donnelly Wash, and Ashurst-Hayden Dam sites contained lead concentrations that exceeded this threshold level.

Mercury was detected in ten of thirteen samples. Mercury concentrations in fish ranged from 0.01 to 0.08 μg/g wet weight (Table 2), all of which were well below the NCBP 85th percentile of 0.17 μg/g. Mercury levels were relatively consistent among sites. Concentrations of mercury in fish appear to have decreased over time in the Donnelly Wash site. The mean mercury concentration in fish collected from the Gila River at Donnelly Wash in 1991-92 was 0.17 $\mu g/g$ (King and Baker 1995). For the protection of sensitive species of birds that regularly consume fish and other aquatic organisms, total mercury concentrations in prey items should not exceed 0.10 $\mu g/g$ wet weight (Eisler 1987). None of the whole body fish samples collected during this study exceeded the 0.10 $\mu g/g$ level of concern. Mercury does not appear to present a contaminant hazard to fish within this portion of the Gila River.

Selenium was present in all fish samples with concentrations ranging from 0.38 to 0.94 $\mu g/g$ wet weight (Table 2). A selenium level of 3.0 $\mu g/g$ dry weight (approximately 0.75 $\mu g/g$ wet weight) is considered potentially lethal to fish and aquatic birds that consume them (Lemly 1993). Only one sample, longfin dace from the Cochran site, exceeded this threshold level. Selenium concentrations of 2.0 $\mu g/g$ wet weight or greater, may cause reproductive impairment and lack of recruitment in fishes (Baumann and May 1984). None of the samples in this study approached this level of concern. Caution should be exercised when comparing selenium levels in fish from this study with the NCBP 85th percentile. The NCBP is subject to regional bias. Because of the widespread occurrence of highly seleniferous soils in western United States, fish from this area contain generally higher selenium concentrations than those of eastern United States. Therefore, we did not attempt to compare our selenium data with those of the NCBP.

Zinc was detected in all fish samples and concentrations ranged from 17.30 to 42.30 $\mu g/g$ wet weight (Table 2). All but three samples contained levels below the

NCBP 85th percentile of 34.2 µg/g. Fish can accumulate zinc from both the surrounding water and from their diet (Eisler 1993). Although zinc is an essential element, at high concentrations, it can be toxic to fish, cause mortality, growth retardation, and reproductive impairment (Sorenson 1991). Zinc is capable of interacting with other elements and producing antagonistic, additive, or synergistic effects (Eisler 1993). The toxicity of zinc is also modified by ambient environmental factors. Zinc is more toxic under conditions of comparatively low dissolved oxygen (Spear 1981) and at elevated temperatures (Spear 1981, Hilmy et al. 1987), common conditions in the desert southwest.

CONCLUSIONS

Copper remains the element of concern in Mineral Creek and downstream portions of the Gila River. Copper concentrations in sediment and fish were elevated at Mineral Creek, then generally decreased in the Gila River with increased distance from the creek. This same trend was evident in sediment and lizards collected in 1991-92 (King and Baker 1995). Although copper concentrations in fish are extremely elevated within Mineral Creek, effects of these levels on biota are not well known. Though lead was elevated in sediment of Mineral Creek, it was not detected in fish from that site. Lead was present in fish from the Riverside, Cochran, Donnelly Wash, and Ashurst-Hayden sites in concentrations that could harm reproduction and survival. Zinc concentrations were elevated in sediment from Mineral Creek and from downstream sites in the Gila River; however, it is not known if these levels are toxic to fish or other aquatic biota.

Concentrations of contaminants in Mineral Creek had clearly been reduced between field investigations in 1993 and 1995 due, in part, to natural revitalization of the creek following a major flood event (1993), and renovations effected by Ray Mine. Before our 1995 collections in Mineral Creek and the Gila River, Ray Mine installed pumpback wells at several locations in an effort to improve the water quality of Mineral Creek. Additionally, the mine installed new pond liners of high density polyethylene and repaired leaks within leach ponds to prevent contaminants from seeping from the ponds into the creek (N. Gambell pers. comm). These measures undoubtedly facilitated the ecological improvement of Mineral Creek from 1993 to 1995.

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Table 1. Trace element concentrations in sediment ($\mu g/g$ dry weight) from the middle Gila River and tributaries, Arizona, 1995.

Site[1]	Al	As	B	Ba	Be	Cd	Cr	Cu	Fe	Hg	Mg	Mo	Mn	Ni	Pb	Se	Sr	V	Zn
Ave.[2]	55213	9.8	NA[3]	565	0.52	NA	61.3	30	NA	0.10	NA	3.0	NA	27.5	23.4	0.30	NA	71.3	62.1
RS	7393	2.79	2.50	82	0.43	<0.23	5.85	44	9344	<0.015	4740	<1.50	433	10.63	8.32	<0.3	83.08	17.84	35.06
MC	34963	17.97	11.37	130	1.65	3.91	29.34	1245	27628	0.042	11173	3.86	597	36.19	72.37	0.49	90.71	46.94	281.17
RW	14682	3.58	3.80	139	1.00	0.39	11.27	128	16747	0.021	8504	1.56	712	16.07	19.84	<0.33	116.10	30.41	78.70
CO	26556	6.93	8.69	185	1.52	0.57	17.16	128	23651	0.048	12365	<1.99	1073	24.07	22.20	0.41	143.15	41.70	91.08

[1] RS - Riverside; MC - Mineral Creek; RW - Ripsey Wash; CO - Cochran
[2] Mean concentration of trace elements in Arizona soils (Boerngen and Shacklette 1981)
[3] NA - Data not available

Table 2. Trace element concentrations (µg/g wet weight) in whole body fish collected from the middle **Gila** River and tributaries, Arizona, 1995.

Sample	Site	Al	AS	B	Ba	Cd	Cr	Cu	**Hg**	Ni	Pb	se	Sr	**Zn**	% Moisture
NCBP	85'	**NA**[2]	0.27	NA	NA	0.05	NA	1.0	0.17	NA	0.22	0.73	NA	34.2	
AGCH[3]	Riverside	837	0.87	0.96	11.4	0.11	1.20	7.58	0.06	1.29	2.34	0.62	27.30	22.0	72.3
LECY[4]	Riverside	3.19	0.08	**<0.4**	0.82	**<0.06**	0.44	0.43	0.07	0.28	0.54	0.39	22.50	19.40	74.9
PACL[5]	Riverside	132	0.58	0.48	2.45	**<0.06**	0.50	3.59	0.08	0.40	**<0.49**	0.75	15.10	34.20	74.7
GAAF[6]	Mineral Creek	66.6	0.06	0.61	0.97	0.24	0.74	14.80	**<0.01**	0.49	**<0.50**	0.52	7.92	38.10	75.1
ICME[7]	Mineral Creek	25.3	**<0.05**	co.4	0.37	0.28	0.28	22.90	**<0.01**	1.75	**<0.50**	0.54	7.84	17.30	80.2
LECY	Mineral Creek	22.2	0.05	0.42	0.61	0.11	0.40	4.85	0.05	0.15	< 0.49	0.38	16.80	26.80	76.5
PACL	Mineral Creek	56.4	**<0.05**	**<0.4**	1.23	0.42	0.33	38.40	**<0.01**	0.33	co.50	0.67	8.51	25.30	76.9
AGCH	Cochran	181	0.4	**<0.4**	2.94	**<0.06**	0.48	3.65	0.05	1.04	< 0.50	0.94	20.10	42.30	72.5
PACL	Cochran	568	1.0	0.93	8.80	0.07	1.49	5.49	0.03	1.96	0.98	0.59	30.70	19.80	71.8
AGCH	Donnelly Wash	329	1.11	0.65	3.98	CO.06	0.63	4.82	0.03	0.59	**<0.50**	0.69	14.80	38.50	69.9
PACL	Donnelly Wash	422	0.83	0.62	7.82	0.11	1.19	5.75	0.03	1.08	0.70	0.60	25.70	18.60	71.3
LECY	A-H Darn”	31.6	**<0.05**	**<0.4**	1.36	**<0.06**	0.50	0.82	0.04	1.18	< 0.49	0.47	24.50	22.70	77.3
PACL	A-H Dam	116	0.14	0.45	4.90	**<0.06**	0.55	4.21	0.01	1.19	< 0.49	0.58	25.0	17.80	72.4

[1] National Contaminant Biomonitoring Program 85th Percentile (Schmitt and Brumbaugh 1990)
[2] NA - Data not available
[3] AGCH - **Longfin dace,** ***Agosia chrysogaster***
[4] LECY - Green sunfish, ***Lepomis cyanellus***
[5] PACL - Desert sucker, ***Pantosteus clarki***
[6] GAAF - Mosquitofish, ***Gambusia affinis***
[7] ICME - Black bullhead, ***Ictalurus melas***
[8] A-H - Ashurst-Hayden