

U.S. Fish and Wildlife Service

Region 2

Contaminants Program

CONTAMINANTS IN FISH AND WILDLIFE
OF THE MIDDLE GILA RIVER, ARIZONA

by

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February 1995

ABSTRACT-Sediment, lizards, and fish collected from 11 middle Gila River sites in 1991-92 contained low levels of organochlorine compounds. Organochlorine compounds were below the threshold levels generally considered hazardous to fish and wildlife. In contrast to organochlorines, some metalloid levels were extremely elevated. Copper was present at 2,660 pg/g dry weight in Mineral Creek sediments; a concentration 89 times higher than the state mean. Molybdenum, selenium, and zinc were also present at elevated levels in Mineral Creek sediments. Aluminum, cadmium, mercury, selenium, and possibly arsenic were detected in one or more lizard samples at concentrations that could cause secondary poisoning of predators that consumed a large proportion of lizards in their diet. Arsenic, cadmium, copper, mercury, and selenium were recovered at above background levels in one or more fish samples; however, the number of fish samples was limited and not representative of the entire study area. Based on consistently elevated metalloid concentrations in sediments, lizards, and fish from Mineral Creek and the Gila River downstream from the creek, future studies should focus on Mineral Creek as a potential source of contamination of the middle Gila River. Several elements were highest in lizards collected from sites downstream from major mining operations. Additional studies are needed to assess potential contaminant input into riparian habitats from mining operations.

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INTRODUCTION

The Gila River bisects southern Arizona flowing from the Arizona-New Mexico border westward to the Arizona-California border. For the purpose of environmental contaminant investigations, the Gila River was divided into three reaches; the upper, middle, and lower Gila. Previous Fish and Wildlife Service (Service) studies identified high levels of metalloids in fish and wildlife resources of the upper Gila River (Baker and King 1994) and above background concentrations of organochlorine compounds in biota of the lower Gila River (Kepner 1987). The purpose of this study was to document contamination levels in sediment, fish, and wildlife of the middle Gila River. This investigation supplements the two preceding studies and completes a contaminant profile of the entire Gila River ecosystem.

STUDY AREA

The middle Gila River is defined as that portion of the river from Coolidge Dam downstream to the Ashurst-Hayden Dam (Fig.1). Potential sources of pollution along this section of the river include municipal discharges, agriculture runoff, and mining. Municipalities and agriculture are confined to the middle third of the study area between Winkelman and Kelvin. Settlements are relatively small with populations $\leq 2,765$. Agriculture is limited due to the rugged topography. Municipal and agricultural contaminant input to the Gila River is minimal (Cox 1976).

Numerous mining operations are scattered throughout the study area. Inspiration Consolidated Copper Company mine at Dripping Springs Wash is the first major mine below Coolidge Dam. A second large mining operation, ASARCO's Ray Mine, is located on Mineral Creek, a tributary to the Gila River. In addition to the mines, two large copper smelters are situated downriver from Winkelman. Toxic substances have been introduced from the mines into the river by direct discharge into tributaries and by runoff of mining wastes (Cox 1976).

Species of special importance include several neotropical migratory songbirds such as the federally proposed endangered southwestern willow flycatcher (*Empidonax traillii extimus*), the yellow-billed cuckoo (*Coccyzus americanus*), a state listed endangered species, and the belted kingfisher *Ceryle alcyon*, a state listed candidate species. The great blue heron (*Ardea herodias*), and common snipe (*Gallinago gallinago*) are also important riparian species common within the study area.

The Gila River and its tributaries represent major lotic waters and important riparian habitats in southeastern Arizona. The Gila River and adjacent flood plain provide a major recreation outlet for local residents. Fishing is popular immediately below

Coolidge Dam. Mourning dove (*Zenaida macroura*), white-winged dove (*Z. asiatica*) and Gambel's quail (*Callipepla gambelii*) are abundant game birds. The

area is valuable for its nongame resources as well. It is popular among bird watchers and wildlife photographers, particularly for its diverse avifauna.

METHODS

Eleven study sites were selected along the middle Gila River and its major tributaries. All samples were collected between June 1991 and May 1992. Five sediment subsamples from approximately the top 5 cm of river bottom were taken at each site using a stainless steel spoon. The five individual samples were placed in a clean stainless steel pan and homogenized into a single composite. The composite sample was then placed in an acid rinsed tared glass jar, weighed, sealed with a teflon lined lid and placed on wet ice until the sample could be transferred to a commercial freezer. The spoon and pan were washed and rinsed with acetone and hexane between collection sites to prevent cross contamination.

Fish were collected by electroshocking and cast net. Fish were weighed and measured then pooled into two- to five-specimen composite samples by species. Whole body fish samples were wrapped in aluminum foil and placed on wet ice until they were transferred to a commercial freezer where they were stored frozen for future chemical analyses.

Whiptail lizards (*Cnemidophorus* spp.) were collected at 10 of 11 sites using a .22 caliber rifle or pistol and lead shotshells. Lizards were weighed and measured then pooled into five specimen composite samples by site. The number of sediment, fish, and lizard samples collected at each site is listed in Table 1.

All samples were analyzed for organochlorine compounds at Hazelton Environmental Services, Inc., Madison, Wisconsin. Organochlorine compounds are expressed in $\mu\text{g/g}$ (parts per million) wet weight.

Sediment, fish, and lizards were also analyzed for aluminum, antimony, arsenic, barium, beryllium, boron, cadmium, chromium, copper, iron, lead, manganese, mercury, molybdenum, nickel, selenium, strontium, vanadium, and zinc. Chemical analyses of sediments and fish were completed at Hazelton Environmental Services, Inc. Lizards were analyzed at Environmental Trace Substance Research Center, Columbia, Missouri. Atomic absorption spectroscopy hydride generation was used to quantitate selenium and arsenic. Mercury concentrations were quantitated by cold vapor atomic absorption. All other elements were analyzed by inductively coupled plasma atomic emission spectroscopy. Analytical methodology and reports met or exceeded Patuxent Analytical Control Facility Quality Assurance and Quality Control standards (Moore 1990). Element concentrations are reported

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in $\mu\text{g/g}$ dry weight for sediment and lizards. Percent moisture is listed in Table 1 for readers who wish to convert sediment and lizard dry weight values to wet weight equivalents. Fish residue data are expressed in both dry weight and wet weight concentrations to facilitate data comparison with published studies.

Element concentrations in sediments were compared with Arizona baseline levels in soils (Boerngen and Shacklette 1991). Since only one composite sample was collected per site, statistical comparisons with background levels are not possible on a site by site basis. If an element concentration exceeded the mean plus two

standard deviations, the concentration was considered significantly ($P < 0.05$) higher than the statewide mean.

Trace element concentrations in fish were compared with those reported in the National Contaminant Biomonitoring Program (NCBP) for fish collected in 1976-1984 from 109 stations nationwide (Schmitt and Brumbaugh 1990). Concentrations of an element in whole fish 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 provides a frame of reference to identify elements of potential concern. There was an insufficient number of sites with fish samples to run statistical comparisons.

RESULTS AND DISCUSSION

The Gila River has been depauperate of both vertebrates and invertebrates since the early 1970s (Kepner et al. 1983). Only two native fish species, longfin dace (*Agosia chrysogaster*) and desert sucker (*Catostomus* [*Pantosteus*] *clarki*), were present in this area in the 1970s (Minckley 1972). During the 1970s, portions of the middle Gila River were virtually devoid of aquatic vertebrates and invertebrates (Stephenson and Ohmart 1974). They stated "the water in the Gila River study area is reddish-golden in color and heavily polluted from industrial waste upstream. The absence of aquatic wildlife in the area appears to be directly related to water pollution."

Almost all water in the middle Gila River is allocated for agricultural use. For several week during winter, water is not released from Coolidge Dam. This annual "dry-down" may have a profound affect on the dynamics of contaminant assimilation by resident fish and wildlife. For most of the year, contaminant loads are governed by flows down the Gila River and releases from Coolidge Dam. During the dry down period, the contaminant profile is influenced for several weeks primarily by bank storage return and by flow from perennial streams such as Dripping Springs Wash, the San Pedro River, and Mineral Creek.

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Although an equal effort was made to collect fish at each site, fish were found only at site 10 (Table 1). Three species were collected; channel catfish (*Ictalurus punctatus*), common carp (*Cyprinus carpio*), and desert sucker. Our fish abundance and diversity data confirm those of Kepner et al. (1983), who reported that the middle Gila River contains relatively poor quality fish habitat. Chronic low fish populations result from continuous high flows that contain a large proportion of suspended sediment. The high flows erase the normal riffle-run-pool heterogeneity which is characteristic of high quality lotic habitat. Normal releases from Coolidge Dam average 459 cfs (Kepner et al. 1983). Under this flow regime, about 95% of the middle Gila River was classified as homogeneous run habitat (USBR 1976).

High sediment loads present during most of the year increase turbidity which reduces photosynthesis. Also, there is a scouring and abrading action by the shifting sediment which precludes the establishment of benthic organisms. Fine sediments bury the stream bottom and create a homogeneous substrate which decreases normal habitat diversity (Kepner et al 1983).

Organochlorine Compounds

Sediments- Organochlorine compounds were not detected in sediments (Table 1). The only organochlorine compound recovered in lizards and fish was p,p'-DDE (DDE). DDE was present in all lizard samples and concentrations varied from 0.01 to 0.06 µg/g wet weight (mean = 0.02 µg/g). DDE in middle Gila River lizards was similar to that (0.01-0.04 µg/g) in lizards collected from the upper portion of the river (Baker and King 1994) but lower than levels in lizards from the lower portion of the river (0.02-4.2 µg/g) between Phoenix and Painted Rock Reservoir (Kepner 1987).

Lizards- Lizards are intermediate predators often consumed by numerous upper trophic level species. Dietary items containing 1.0 µg/g DDT family compounds represent the upper limit for protection of wildlife (Nat. Acad. Sci. & Nat. Acad. Engineers 1973). DDE in lizards from the middle Gila River should not present a bioaccumulation hazard to predators that consume them.

Fish- DDE was the only organochlorine compound recovered in fish. Carp and channel catfish contained 0.05 and 0.03 µg/g wet weight DDE, respectively. DDE in desert sucker, if present, was less than the detection limit of 0.01 µg/g. The maximum concentration of DDE in fish, 0.05 µg/g wet weight, was well below the NCBP geometric mean of 0.19 µg/g which represents the background level of DDE in fish (Schmitt et al. 1990).

Birds- Many species of fish-eating birds are susceptible to DDE-induced egg shell thinning and reproductive failure. Dietary levels of 0.6 to 3.0 µg/g wet weight DDE can result in a significant degree of eggshell thinning in a variety of species (McLane and Hall 1972, Stickel 1973, Longcore and Stendell 1982). The maximum

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level of DDE detected in fish from this study was well below the shell thinning concern level.

Metal bids

Sediment- Nineteen elements were detected in sediment samples (Table 2). Most elements were close to, or below Arizona background levels in soils (Boerngen and Shacklette 1991). The notable exception was copper. Copper was present at significantly (mean + 2 standard deviations) higher than background levels in sediments from 8 of 11 sites. The highest concentration, 2,660 µg/g, was present in Mineral Creek sediments and was almost 90 times the state mean of 30 µg/g copper. The four Gila River sites downstream of its confluence with Mineral Creek were also contaminated with copper (Fig. 1, Table 2). Only three other elements, molybdenum, selenium, and zinc, were detected in sediments at concentrations significantly greater than the state mean. Each element was present at elevated levels only in sediments from Mineral Creek (Table 2).

Lizards- Whiptail lizards are terrestrial and obtain little, if any, of their contaminant burden through the aquatic food chain. Lizards, never-the-less are excellent indicators of local contamination. Much of their diet consists of small invertebrates of local origin. Lizards also ingest a significant amount of soil along with their diet.

In a study of soil ingestion in a variety of wildlife species, birds incidentally consumed up to 30% soil through their diet, mammals consumed up to 17%, and the box turtle (*Terrapene carolina*), the only reptile studied, ingested 4% soil with its diet (Beyer et al. 1994).

Seventeen of 19 trace elements were detected in lizards (Table 3). Because of highly variable concentrations of certain elements in some samples, the elemental content of "lead" shotshells was questioned. There was a possibility that some samples were contaminated by elements other than lead in the shot. An analysis of a composite sample of shot from five shotshells indicated that the "lead" in shotshells also contained arsenic (4,447 $\mu\text{g/g}$), boron (11 $\mu\text{g/g}$), cadmium (1.8 $\mu\text{g/g}$), copper (65 $\mu\text{g/g}$), and iron (5.2 $\mu\text{g/g}$). Because environmental levels of iron were relatively high ($\approx 250 \mu\text{g/g}$) in lizards, the additional tissue contamination from shot would be insignificant. The high level of probability that lizards collected with shotshells were contaminated by arsenic, boron, cadmium, and copper from the shot makes interpretation of residue data difficult. Data for these elements are presented in Table 3 for information purposes only.

Almost no data are available on "normal" or background levels of trace elements in whole body lizards. Therefore, information gathered in this study along with other Arizona investigations (Baker and King 1994) will establish a baseline for elemental levels in whole body lizards.

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Some metalloids in lizards may be harmful to predators that consume a significant proportion of lizards in their diet. Elements most likely to be toxic to bird and mammal predators include aluminum, arsenic, cadmium, mercury, and selenium. The maximum tolerable aluminum concentrations in the diet of domestic animals varies from 200-1,000 $\mu\text{g/g}$ dry weight (National Research Council 1980). Flycatchers feeding on insects that contained 1,230 $\mu\text{g/g}$ dry weight aluminum experienced severe eggshell defects, reduced clutch size, and a high incidence of mortality (Nyholm and Myhrberg 1977, Nyholm 1981). Juvenile doves fed up to 1,500 $\mu\text{g/g}$ dry weight aluminum for 63 days demonstrated no growth impairments. Aluminum was detected at $\approx 1,200 \mu\text{g/g}$ dry weight in two lizard samples (Table 3). At this concentration, aluminum was within the range associated with reproductive failure of flycatchers but below concentrations associated with growth impairment of doves.

Arsenic was detected in shot used to collect lizards at over 4,400 $\mu\text{g/g}$; therefore, tissue data are biased because of the possibility that lead shot may have been retained in the carcasses. It is interesting to note, however, that the sites with the two highest arsenic concentrations are sites one and seven; sites where aluminum was highest. The Cyprus Miami Copper mine is located upstream (Dripping Springs Wash) from collection site one and Ray Copper Mine is located upstream (Mineral Creek) from site seven.

Cadmium was recovered in lizards from 8 of 11 locations. Secondary hazards of cadmium poisoning to predators may be expected if dietary levels reach 0.1 $\mu\text{g/g}$

wet weight (Eisler 1985), or about 0.36 µg/g dry weight assuming 72% average moisture. Lizards collected from 4 of 10 sites contained cadmium in excess of the concern level.

Copper was present in the shotshells at 65 µg/g. Only one lizard sample, the sample from site 7 contained copper at a level greater than that detected in the shot. Although some of the copper detected in this sample may have originated in the shotshells, much of the 87.8 µg/g must be environmental copper.

The minimum mercury concentration which may cause effects on predatory birds is 0.1 µg/g wet weight (Eisler 1987), or approximately 0.36 µg/g dry weight. In mammals, the hazardous level is 1.1 µg/g wet weight (Eisler 1987), which is comparable to 3.9 µg/g dry weight. Two of 10 lizard samples contained environmental mercury in excess of the avian concern level of 0.36 µg/g. There is no lizard-mercury hazard to mammalian predators.

Selenium levels in lizards varied from 0.9 to 2.9 µg/g dry weight (Table 3). The level of concern for selenium in the food chain of birds and mammals is between 2-6 µg/g dry weight (Hoffman et al. 1991, Skorupa and Ohlendorf 1991). "Normal" food chain selenium levels in an aquatic environment are \leq 2.0 µg/g dry weight

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(Ohlendorf et al. 1990), but little comparable data are available for selenium in terrestrial food chains. Seven of 10 lizard samples contained > 2.0 µg/g selenium dry weight. The 2.9 µg/g concentration in one lizard sample approached the 3.0 µg/g dry weight level that may be reproductively lethal to some bird species (Lemly 1993).

Fish- We are hesitant about making contaminant-fish generalizations because we were able to collect fish from only one location. The following summary applies to fish collected at site 10. Thirteen elements were detected in both channel catfish and carp and 16 elements were present in desert sucker (Table 4). Sucker accumulated several elements to higher levels than other fish. Aluminum, boron, barium, cadmium, copper, iron, manganese, nickel, and vanadium in sucker varied from 2- to 8-times concentrations detected in channel catfish and carp. Mercury, selenium, and zinc were greatest in carp.

Nationwide background or "normal" concentrations of arsenic, cadmium, copper, mercury, selenium, and zinc were documented for fish during the NCBP (Schmitt and Brumbaugh 1990). Arsenic was elevated (> NCBP 85th percentile) in channel catfish and desert sucker samples (Table 4). Cadmium was present at above background levels only in desert sucker. Copper in channel catfish was below the NCBP 85th percentile; but, copper was two-times greater than background levels in carp, and four-times greater than background levels in desert sucker. Mercury was present at above background levels only in carp. Selenium levels were within the background range in channel catfish and sucker; but, selenium was slightly elevated in carp. None of the fish samples contained above background levels of zinc.

Residue implications for fish-eating birds- Metals and metalloids most likely to cause reproductive problems in birds are arsenic, cadmium, mercury and selenium (Eisler 1985, 1987, 1988; Ohlendorf et al. 1986, 1988). While the acute effects of

arsenic have been investigated, little is known about its sublethal chronic effects except that arsenic is readily accumulated by aquatic organisms. Based on data summarized by Eisler (1988), arsenic at concentrations recovered in Gila River fish from site 10 apparently poses little hazard of secondary poisoning to avian predators. Secondary hazards of cadmium poisoning to avian predators might be expected if dietary intake reaches 0.1 µg/g wet weight (Eisler 1985) but cadmium was less than 0.1 µg/g in all fish samples. The maximum concentration above which mercury effects fish-eating avian predators is about 0.1 µg/g wet weight (Eisler 1987). All fish samples contained mercury at concentrations in excess of the 0.1 µg/g concern level (0.12-0.26 µg/g). Therefore, birds consuming a large proportion of fish in their diet may be in danger of bioaccumulating potentially hazardous concentrations of mercury. "Normal" food chain selenium levels in an aquatic environment are 0.2 µg/g dry weight (Ohlendorf et al. 1990). Organisms containing 3 ppm (dry weight) or more should be viewed as potentially lethal to fish

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and aquatic birds that consume them (Lemly 1993). Only the carp sample contained selenium at levels (4.09 µg/g dry weight) potentially hazardous to predators.

Although copper concentrations in fish were two to four times background levels, there is little potential for bioaccumulation of copper to hazardous concentrations because copper is considered a nutritionally essential element and is relatively non-toxic to warm blooded animals.

RECOMMENDATIONS

Based on exceedingly high metalloid residues in the lower portion of the study area, we recommend future study of Mineral Creek as a potential source of contamination of the Gila River. The two study sites with consistently high levels of most elements were Mineral Creek (site 7) and the Gila River site just downstream from Mineral Creek (site 8). Copper was present in Mineral Creek sediments at 89-times background levels; molybdenum, selenium, and zinc were detected at elevated concentrations only at the Mineral Creek site. Lizards collected adjacent to Mineral Creek had extremely elevated levels of copper. One or more fish samples from site 10, downstream from Mineral Creek, contained elevated arsenic, cadmium, copper, mercury, and selenium. Future studies should focus on contaminant impacts to flora and fauna in and near Mineral Creek and in downstream Gila River habitats. This portion of the Gila River contains habitat for the (proposed) endangered southwestern willow flycatcher (*Empidonax traillii* extimus) and provides important nesting, migrating, and wintering riparian habitat for numerous neotropical songbirds. Potential contaminant impacts to the flycatcher and songbirds should be identified.

Several elements were highest in lizards collected from sites one and seven, downstream from major copper mining operations. Additional studies are needed to assess potential contaminant input into riparian habitats from mining operations.

ACKNOWLEDGEMENTS

We thank Marc Dahlberg, Todd Pringle, Bill Watt, Elaine Johnson, Kathy Linder, and Julie Fulkerson for assistance with field work. This report was reviewed by

Mark Wilson, Cynthia Martinez, Brenda Andrews, and Frank Baucom who made numerous helpful and constructive comments. Appreciation is also expressed to Don Henry for assistance with computer graphics.

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[See Table/Figure](#)

Figure 1. Collection site locations, middle Gila River, 1991-1992.

Table 1. Organochlorine residues (æg/g wet weight) in sediment, lizards and fish collected from the middle Gila River, Arizona 1991-92|

Site No.	Sample	N ^{[sup]b}	Weight (g)	Prcnt moist	Prcnt lipid	p,p'-DDE
1	Sediment	5	139	57.67	NA	<0.01
2	Sediment	5	163	42.39	NA	<0.01
3	Sediment	5	126	37.33	NA	<0.01
4	Sediment	5	132	34.30	NA	<0.01
5	Sediment	5	146	44.39	NA	<0.01
6	Sediment	5	124	53.42	NA	<0.01
7	Sediment	5	123	34.0	NA	<0.01
8	Sediment	5	101	37.29	NA	<0.01
9	Sediment	5	142	26.66	NA	<0.01
10	Sediment	5	156	40.21	NA	<0.01
11	Sediment	5	166	28.63	NA	<0.01
1	Lizard	5	63	71.0	3.72	0.01
2	Lizard	5	88	69.5	5.42	0.02
4	Lizard	5	63	69.5	5.76	0.01
5	Lizard	5	45	73.0	2.36	0.04
6	Lizard	5	45	71.5	3.64	0.02
7	Lizard	5	45	72.0	2.42	0.06
8	Lizard	5	54	72.0	2.96	0.01
9	Lizard	5	89	71.93	2.11	0.01
10	Lizard	5	69	70.04	1.86	0.01
11	Lizard	5	72	73.65	1.6	0.01
10	C carp ^{[sup]c}	2	2723	72.86	6.42	0.05
10	D sucker ^{[sup]c}	5	247	71.7	13.19	<0.01
10	C catfish ^{[sup]c}	2	556	71.96	9.01	0.03

|The lower limit of detection (LLD) for organochlorines in

sediments was 0.01 µg/g wet weight for all compounds except PCB. PCB LLD= 0.1 µg/g. LLD for organochlorines in tissues was 0.01 µg/g wet weight for all compounds except toxaphene and PCB (LLD= 0.05 µg/g).

[sup]bN= number of individuals in each composite sample.

[sup]cFish abbreviations; C carp= common carp, D sucker= desert sucker, C catfish= channel catfish.

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Table 2. Trace elements in middle Gila River sediments[¹]

[See Table/Figure](#)

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Table 3. Trace elements in whiptail lizards collected from the middle Gila River area, Arizona, 1991-92

[See Table/Figure](#)

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Table 4. Trace elements in fish collected from the middle Gila River, Arizona, 1991-92[¹]

[See Table/Figure](#)